Enhancing the Air Stability of Dimolybdenum Paddlewheel Complexes: Redox Tuning through Fluorine Substituents

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Abstract: The optical and electrochemical properties of quadruply bonded dimolybdenum paddlewheel complexes (Mo₂PWCs) make them ideal candidates for incorporation into functional materials or devices, but one of the greatest bottlenecks for this is their poor stability toward atmospheric oxygen. By tuning the potential at which the Mo₂ core is oxidized, it was possible to increase the tolerance of Mo₂PWCs to air. A series of homoleptic Mo₂PWCs bearing fluorinated formamidinate ligands have been synthesized and their electrochemical properties studied. The oxidation potential of the complexes was tuned in a predictable fashion by controlling the positions of the fluorine substituents on the ligands, as guided by a Hammett relationship. Studies into the air stability of the resulting complexes by multinuclear NMR spectroscopy show an increased tolerance to atmospheric oxygen with increasingly electron-withdrawing ligands. The heteroleptic complex Mo₂(D₅ArF)₃(OAc) [where D₅ArF = 3,5-(difluorophenyl)formamidinate] shows remarkable tolerance to oxygen in the solid state and in chloroform solutions. Through the employment of easily accessible ligands, the stability of the Mo₂ core toward oxygen has been enhanced, thereby making Mo₂PWCs with electron-withdrawing ligands more attractive candidates for the development of functional materials.

Introduction: Quadruply-bonded dimolybdenum paddlewheel complexes (Mo₂PWCs) have enormous potential as components for functional materials. Their 3D structure allows the construction of large molecular arrays through combination with a broad scope of bridging ligands.¹⁻³ They are redox-active, undergoing one-electron oxidation processes, often at easily accessible potentials. Additionally, the strong interaction between the Mo₂δ and π systems of equatorial chelating ligands (e.g., carboxylates (-O₂CR) and formamidinates (−NN; Figure 1)) is ideal for facilitating and studying electron transfer in mixed-valence architectures²⁻⁸ and in photoexcited states.⁹,¹⁰ Consequently, Mo₂PWCs are starting to find application in solar energy conversion,¹¹,¹² molecular electronics,¹³ and catalysis.¹⁴,¹⁵ However, there is one important caveat. Mo₂PWCs are air-sensitive,¹⁶ reacting readily with atmospheric oxygen (O₂), which could be seen as problematic for their translation into the aforementioned technologies. Therefore, a family of air-tolerant dimolybdenum compounds that could be further functionalized toward an intended application is highly desirable. One of the most stable Mo₂PWCs is Mo₂(OAc)₄, which in its crystalline state is stable under an ambient atmosphere for around 1 week before visible discoloration occurs. The origin of this increased air stability stems from intermolecular Mo−O axial interactions that propagate through the material and hinder the approach of oxygen.¹⁷ Thus, using either Lewis basic or sterically bulky ligands to protect the axial position of the paddlewheel complex could be a viable method for enhancing the air stability.

An alternative approach toward increasing O₂ tolerance, and the focus of this study, is to increase the oxidation potential of.
the metal core such that the reaction with O$_2$ becomes thermodynamically unfavorable.\textsuperscript{18} Tuning the oxidation potential of paddlewheel complexes can be achieved primarily by systematic variation of the ancillary ligands. In the homologous series Mo$_3$(D,C,C$\equiv$C$\equiv$C-P$_{Ph}$)$_4$, where the donor atoms (D) were NN, ON, NS, and OO, the oxidation potential of the Mo$_3$PWCs in NN-dimethylformamide solutions could be tuned between $-0.322$ V (NN donor) and $+0.282$ V (OO donor), a range of 0.6 V.\textsuperscript{19} The hpp ligand (where H$_{hpp}$ = 1,3,4,6,7,8- hexahydro-2H-pyrimido[1,2-a]pyrimidine) is a strong Lewis base and has been used to stabilize the W$_6^{6+}$ core in the most easily ionizable complexes known.\textsuperscript{20} Recently, the hpp ligand has been employed alongside formamidinate ligands to tune the Mo$_{60}^{4+}/_2$ couple from $-0.381$ V in Mo$_3$(DAniF)$_4$ [DAniF$^-$/di-4-anisylformamidinate] to potentials as low as $-1.795$ V versus ferrocene/ferrocenium (Fc/Fc$^+$) in Mo$_3$(hpp)$_4$. Remote substituents on the ligands can also influence the properties of the dimetal core. This was illustrated as a linear free-energy relationship between the Hammett constant of the ligand substituents and the oxidation potential of the Mo$_2$ core in a family of homoleptic formamidinate complexes, Mo$_2$(NN)$_4$$_{[a]}$ (where $E_{1/2}(p$-OMe) = 0.244 V through to $E_{1/2}(p$-CF$_3$) = 0.795 V vs Ag/AgCl) [Figure 1].\textsuperscript{21} Interestingly, the UV/visible spectrum (in CH$_2$Cl$_2$) of species with the strongest electron-withdrawing substituents ($3.5$-Cl$_2$, $2n_m = 0.74$) remained unchanged, even after being exposed to air for 1 week.\textsuperscript{22} The same free-energy relationship was also observed between remote substituents on the ligands and the extent of charge stabilization ($\Delta E_{1/2}$) in mixed-valence dimers, of the form [Mo$_2$(NN)$_{1,2}$]$_2$(µ-O$_2$CC$_6$H$_4$CO$_2$)$_2$.\textsuperscript{23} The electronic properties of Ru$_2$PWCs can also be varied with fluorinated ancillary ligands, which has been shown on multiple occasions.\textsuperscript{24–27} In one particular example, fluorinated and chlorinated benzoates were employed to achieve a remarkable fine-tuning of the oxidation potential of Ru$_2$PWCs between $-0.039$ and $0.36$ V vs Fc/Fc$^+$ in tetrahydrofuran (THF).\textsuperscript{28} Indeed, the authors also noted that those species with $E_{1/2} > 0.3$ V showed increased stability to O$_2$.

Substituted formamidinates and benzoates have both been shown to effectively tune the properties of paddlewheel complexes\textsuperscript{29,30} and clusters.\textsuperscript{31,32} However, there has not yet been a systematic study employing fluorinated formamidinates to control the properties of Mo$_3$PWCs. Fluorine is the ideal substituent to tune Mo$_3$PWCs for several reasons. First, it is the most electronegative element with a considerable electron-withdrawing effect ($\sigma_F = 0.062$; $\sigma_m = 0.337$). Other functionalities such as cyano ($\sigma_m = 0.56$) or nitro ($\sigma_m = 0.71$) groups may exhibit stronger electron-withdrawing effects, but they are also potentially reactive, which may limit further application of the complexes. In contrast, the C–F bond is exceptionally strong, with a bond dissociation energy of 127.2 ± 0.7 kcal mol$^{-1}$ in fluorobenzene (C–H in benzene is 112.9 ± 0.6 kcal mol$^{-1}$), meaning that any subsequent complexes are unlikely to undergo deleterious side reactions at the ligand periphery.\textsuperscript{33} Second, the fluorine atom is small, with an atomic radius (vdW = van der Waals) only slightly larger than that of hydrogen ($r_{\text{vdW}}$: F = 1.47 Å; H = 1.20 Å). Thus, the substitution of protons with fluorine atoms will have the minimal steric influence on the overall structures, unlike chloro analogues, which are significantly larger ($r_{\text{vdW}} = 1.75$ Å).\textsuperscript{33} In one report, a family of homoleptic dichromium tetraformamidinates with various fluorine-substitution patterns were studied, and it was found that the fluorination pattern had no influence on the Cr–Cr bond length of the complexes.\textsuperscript{30} Finally, the $^{19}$F nucleus is NMR-active with 100% natural abundance $I = 1/2$ and so provides a useful quantitative probe for NMR spectroscopic characterization or a further study of molecular dynamics. We envision that Mo$_3$PWCs bearing kinetically inert\textsuperscript{34} formamidinate ligands with carefully selected fluorination patterns would represent a powerful approach toward achieving Mo$_3$PWCs with enhanced air stability and therefore have the potential to be translated into functional materials. Using Hammett constants ($\sigma$) as a guide, we demonstrate that we can predictably tune the electronic properties (specifically the oxidation potential) of Mo$_3$PWCs by varying the positions and quantity of fluorine atoms on the formamidinate ligands. We also employ NMR spectroscopy as a tool to follow decomposition of the complexes and demonstrate an increased tolerance to atmospheric oxygen with increasing $\sigma$. We also demonstrate that this strategy can be applied to heteroleptic complexes [Mo$_3$(NN)$_3$(OAc)$_x$], which are key synths for accessing functional materials.

## RESULTS AND DISCUSSION

### Synthesis. Ligand Design, Synthesis, and Characterization

In the chemistry of Mo$_3$PWCs, carboxylate ligands are known to be kinetically labile (particularly if they bear strong electron-withdrawing groups),\textsuperscript{35,36} whereas formamidinate ligands are more persistent because of their increased Lewis basicity.\textsuperscript{34} Therefore, formamidinates are arguably more desirable ligand choices in the pursuit of robust functional materials. With that in mind, a family of formamidinate ligands with different fluoride-substitution patterns were synthesized. All formamidinate ligands described herein, including novel compounds 1d and 1e, can be synthesized following a well-established condensation reaction between the corresponding aniline and triethylthioformate (Figure 2),\textsuperscript{27} generating off-white microcrystalline solids in yields varying from 50 to 80%. Each ligand has been characterized by $^1$H and $^{19}$F NMR spectroscopy in acetone-$d_6$, electrospray ionization mass spectrometry (ESI MS), and elemental analysis, and in the case of 1c–1f, single-crystal X-ray structures have been obtained and are displayed in the Supporting Information (SI). Single crystals were obtained from either recrystallization of the compound in toluene/hexane (2:1) or by vapor diffusion of hexane into a toluene solution. Compounds 1c–1e all crystallize in an E-syn conformation where the aryl groups point away from the NCN bridge.\textsuperscript{37} However, 1f buckles considerably and adopts the E-anti configuration, presumably to minimize any steric interaction between the e-fluorine atoms on the rings, although the E-syn configuration is still observed in the reported crystal structure of 1h.\textsuperscript{38} Notably, for compounds 1c–1f, we observe intermolecular hydrogen bonding in the packing of the single-crystal solid-state structure.

The synthesis of homoleptic paddlewheel complexes of the form Mo$_3$(NN)$_x$ can be achieved either by (i) reacting the free ligand (1x) with Mo(CO)$_5$ at ca. 160 °C or (ii) by reacting anionic ligand salts (i.e., Li-1x) with Mo$_3$(OAc)$_x$ at room temperature.\textsuperscript{37} We exclusively employ route (i) as described in Scheme 1, and although the yields appear low (9–30%), they are comparable to those from route (ii) when the synthesis of Mo$_3$(OAc)$_4$ from Mo(CO)$_5$ is factored in. The heteroleptic complex 3c was synthesized by reacting Mo$_3$(OAc)$_4$ with exactly 3 equiv of 1c in THF and exactly 3 equiv of NaOMe in MeOH.\textsuperscript{39} Deviation from exact quantities will generate
intractable mixtures of 3c with either the tetraformamidinate (2c) or bisformamidinate complexes. All compounds present as canary-yellow solids with varying degrees of solubility in organic solvents, although THF will dissolve all but 2h. In general, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) showed a molecular ion ([M]+) for each compound at the expected m/z values, and the 1H and 19F NMR spectra displayed the resonances expected for each species. However, in most of the homoleptic complexes, the MALDI-TOF MS spectrum displayed an additional feature with an m/z value 88 units higher than the molecular-ion peak, which can be attributed to a Lewis adduct of some kind, where the Lewis base is coordinating to the axial site of the Mo2 unit. This adduct signal appears to be absent from the MALDI-TOF MS spectrum of 2h, which features the most sterically demanding ligand in the series. The 1H and 19F NMR spectra also suggest evidence for adduct formation, although to varying extents within the series; compound 2c provides the clearest example of this (Figures S31 and S32). At this point, the identity of this Lewis base remains unclear, but simulating an additional C3H4O2 to the mass of the expected molecular-ion fits well with the experimental observations. This would suggest either dioxane or ethyl acetate, but because neither of these compounds was included in the synthetic procedure, we can only speculate as to their origin. Regardless, this observation hints strongly at the potential for these compounds to act as Lewis acids, which may have downstream applications in catalysis.

**Molecular Structure.** Crystals suitable for X-ray diffraction (XRD) studies were obtained for compounds 2b–2j (Figure 3). In most cases, crystals were obtained by the slow diffusion of hexane into a THF solution of the complex. However, 2g crystallized by cooling a hot saturated 1,2-difluorobenzene (DFB) solution, and 2e was crystallized by the slow diffusion of hexane into a DFB solution of the complex. The unit cells exhibited a range of symmetries that indicate the sensitivity of the packing structure to the nature of the arene substitution pattern and the solvent system that the crystal was grown from. Importantly, none of the structures showed evidence of axial coordination, although many did crystallize with solvent molecules in interstitial sites. The Mo–Mo bond lengths occur in the range 2.0924(7)–2.1035(13) Å, placing these complexes within the normal range for Mo2PWCs (Table 1).42

In a series of previously reported terephthalate-bridged “dimers of dimers”, [Mo2(NN)]3(μ-O2CC6H4CO2) where NN = para-functionalized diarylformamidinate ligands, the Mo–Mo bond length was found to decrease with the electron-withdrawing ability of the para substituent. However, in a series of homoleptic formamidinate complexes, the remote substituents appeared to have little influence on the geometry about the dimolybdenum core.41 Using the data collected herein, the Mo–Mo and average Mo–N bond lengths were plotted against the Hammett constants for each ligand, defined as

\[
\sum n(x\sigma_m + y\sigma_p),
\]

where \(n\) is twice the number of formamidinate ligands (i.e., 2 \times 4 for 2x and 2 \times 3 for 3c), \(\sigma_m\) = -F = 0.337, \(\sigma_p\) = F = 0.062, \(\sigma_m\) = CF3 = 0.43, \(\sigma_p\) = CF3 = 0.54, and \(x\) and \(y\) represent the number of meta and para substituents, respectively. However, in this case, no observable trend is apparent in the Mo–Mo and Mo–N distances across the series. It is important to note that Hammett parameters do not account for substituents in an ortho position because the steric effects of the substituent can influence the observed parameters. Removing compounds containing o-fluoro substituents (2d–2f and 2h) from the data analysis did not lead to a stronger positive correlation between the Hammett parameter and the bond lengths, as determined by \(R^2\) in a least-squares fit analysis.

Curious to see if these observations were largely a consequence of packing effects, the optimal geometries of the complexes in the gas phase were calculated using density functional theory (DFT) with the B3LYP functional and def2-SV(P) basis set. The resulting Mo–Mo bond lengths (Table 1) were plotted versus the Hammett constants as above (Figure 4). At first glance, there appeared to be only a weak positive correlation between the Mo–Mo bond lengths and Hammett constants. However, excluding species containing o-fluorine substituents (2d–2f and 2h) from the data led to a...
much stronger correlation ($R^2 = 0.9873$). The large difference in the calculated Mo–Mo bond length between 2d and 2e is surprising considering the similarity of their electronics, so there is likely a significant steric influence at play. Interestingly, there also appears to be a similar discrepancy in the crystallographic data for these compounds, but because they were grown from different solvent systems and have different space groups, it is hard to draw meaningful conclusions from that observation. These calculations suggest that remote substituents can have a significant influence on the length of the quadruple bond, although crystal packing effects dominate the solid-state geometries. This also highlights that, even though the vdw radius of fluorine is small, it, nevertheless, exerts a significant steric influence on the overall molecular structure when occupying the ortho position. Similarly, regardless of how the data were selected, there was no correlation between the ligand substituents and average Mo–N bond lengths for either the crystallographic or calculated data. The Mo–Mo bond length in 3c was calculated to be notably shorter than any in the 2x series, and this trend was also observed in other comparisons of homoleptic Mo$_2$(NN)$_4$ versus heteroleptic Mo$_2$(NN)$_3$(OAc) complexes in the literature. Formamidinate ligands are primarily $\pi$ donors,

**Figure 3.** Visualizations of the X-ray crystal structures of compounds 2b–2j. Hydrogen atoms and solvents of crystallization are removed for clarity, and thermal ellipsoids are reported at 50% probability. For disordered components, the highest occupancy conformation is shown. Color code: gray, carbon; lilac, nitrogen; teal, molybdenum; lime green, fluorine.

Table 1. Mo–Mo Bond Lengths for Complexes 2a–2j Obtained from Experimental Crystallography Data or from Gas-Phase Quantum-Chemical Calculations [DFT and B3LYP/def2_SV(P)]

| compound | crystallographic Mo–Mo bond length/Å | crystallographic average Mo–N bond length/Å | calculated Mo–Mo bond length/Å | calculated average Mo–N bond length/Å |
|----------|-----------------------------------|------------------------------------------|-----------------------------|-------------------------------------|
| 2a       | 2.0944(8)$^a$                     | 2.1582[15]$^a$                          | 2.0816                      | 2.1882                              |
| 2b       | 2.0934(7)                         | 2.1577[24]                              | 2.0816                      | 2.1868                              |
| 2c       | 2.0992(7)                         | 2.1617[7]$^a$                           | 2.0804                      | 2.1883                              |
| 2d       | 2.1024(12)                        | 2.1674[18]                              | 2.0802                      | 2.1886                              |
| 2e       | 2.0999(52)                        | 2.1579[14]                              | 2.0894                      | 2.1936                              |
| 2f       | 2.1022(59)                        | 2.1693[19]                              | 2.0877                      | 2.2016                              |
| 2g       | 2.0924(7)                         | 2.1574[21]                              | 2.0804                      | 2.1871                              |
| 2h       | 2.0999(7)                         | 2.1765[10]                              | 2.0871                      | 2.2025                              |
| 2i       | 2.1035(13)                        | 2.1624[47]                              | 2.0806                      | 2.1891                              |
| 2j       | 2.0952(8)                         | 2.1630[2]                               | 2.0802                      | 2.1886                              |
| 3c       | 2.0766                            | 2.1674                                  | 2.1370                      | (Mo–O)                              |

$^a$Obtained from ref 21.

**Figure 4.** Least-squares regression plot showing the relationship between the calculated Mo–Mo bond length (Å) and Hammett constant. Blue data points contain one $o$-fluorine per arene, and gray data points contain two. $R^2$ was calculated by excluding datapoints 2d–f and 2h.
meaning that the ligands donate electron density to the \( \delta^* \) orbital on the Mo\(_3\) core, thus lengthening the Mo–Mo bond. Therefore, the shorter Mo–Mo bond length in 3c versus 2c can be rationalized as simply a case of fewer ligands donating to the \( \delta^* \) orbital.

**Electronic Structure.** Using the optimized geometries for complexes 2a–2j, single-point calculations were performed using the PBE0 functional and def2-TZVPP basis set to interrogate the frontier molecular orbitals. The frontier molecular orbitals for all complexes can be found in Figures S96–S106. As is characteristic of most Mo\(_2\)PW\(_6\)Cs, the highest occupied molecular orbital (HOMO) in each case is observed to be largely Mo\(_3\)-\( \delta \) in character with out-of-phase mixing with the carbon-based \( p \) orbital on the NCN bridge of the formamidinate ligand. The lowest unoccupied molecular orbital (LUMO) in each case is largely Mo\(_3\)-\( \delta^* \) but with a little mixing of the \( \pi^* \) orbitals of the formamidinate ligands.

Natural bond orbital (NBO) analysis performed on complexes 2a–2j and 3c showed the % Mo\(_2\)-\( \delta \) character to be consistent throughout the series, contributing 87–88% and 86% to the HOMO, respectively. The strong electron-withdrawing nature of the fluorine substituents is sufficient to reduce the electron density donated from the formamidinate ligands onto the dimolybdenum core, and thus the Mo\(_2\)-\( \delta \) orbital is stabilized to an extent that is largely determined by the Hammett constant of the ligands (Figure 5). Importantly, the Mo\(_2\)-\( \delta^* \) orbital is also stabilized to a similar extent across the series, and, consequently, there is only a slight variation in the HOMO–LUMO energy gap, which averages out at 3.51 eV. The same trend was reported in the earlier studies on Mo\(_2\)(NN)\(_3\) complexes with an average HOMO–LUMO gap of 4.78 eV,\(^{21}\) but it is likely that these energies differ only as a consequence of employing different computational methods. This consistency of the HOMO–LUMO gap across the series can also be observed experimentally. By eye, each compound is a very similar light-yellow powder, and the UV/visible absorption spectra typically show a weak transition at ca. 410 nm, which can be assigned as the Mo\(_2\)-\( \delta \) → \( \delta^* \) transition. This assignment is supported by quantum-chemical calculations using time-dependent DFT (TD-DFT), which showed that the lowest-energy excitation of complexes 2a–2j could be identified nearly exclusively as the HOMO–LUMO transition in all complexes. Additionally, the energy of this transition was calculated to be similar for all complexes, with less than 30 nm variation across the series. The higher-energy transitions in the absorption spectrum (<300 nm) are more intense and can be assigned as combinations of Mo\(_2\)-\( \delta \) → ligand-\( \pi^* \) metal-to-ligand charge-transfer and ligand-based \( \pi \)–\( \pi^* \) transitions. These assignments are also supported by TD-DFT analysis.

![Figure 5](image)

**Figure 5.** Least-squares regression plot showing the relationship between the calculated energy (PBE0/def2-TZVPP) of the frontier molecular orbitals for compounds 2a–2j and their corresponding Hammett constants (assuming \( \sigma_{ortho} = 0 \)). \( R^2 \) values were calculated without including data for 3c.

Furthermore, the shortest Mo–Mo bond is 3.74 Å in 2c, and hence the Mo–Mo bond is lengthened. This effect is seen in the charge densities of the formamidinate ligands.

**Data:**

| Compound | Mo–Mo Bond (Å) | HOMO Energy (eV) | LUMO Energy (eV) | HOMO–LUMO Gap (eV) |
|----------|----------------|------------------|------------------|--------------------|
| 2a       | 3.43           | -5.55            | -7.30            | 1.75               |
| 2b       | 3.45           | -5.58            | -7.35            | 1.77               |
| 2c       | 3.74           | -5.60            | -7.60            | 1.80               |

**Conclusion:**

As expected, \( E_{1/2} \) for the complexes in this series largely mirrors the relationship calculated for the HOMO energies. For example, compound 2b contains only a single fluoride atom in the para position per aryl group and has an overall Hammett constant of \( \sigma = 0.5 \). In this case, there is little perturbation of the HOMO energy, and thus oxidation of the Mo\(_2\) core occurs at relatively low potentials (\( E_{1/2} = 31 \) mV). Conversely, compound 3c has two fluoride atoms occupying the meta positions on each aryl, with an overall Hammett constant of \( \sigma = 5.4 \). In this case, there is significant stabilization of the HOMO energy, which makes the complex much harder to oxidize (\( E_{1/2} = 335 \) mV). Figure 8 was constructed under the assumption that \( \sigma_{ortho} = 0 \). Compounds 2d and 2e both have a single \( \sigma \)-fluorine substituent on each ring, while compound 2f has two on each ring. These clearly have an influence on the redox potential of the Mo\(_3\) core, particularly in a comparison of 2b and 2f, which are formally assigned with the same Hammett constant (\( \sigma = 0.5 \)). In previous reports of a family of fluorinated diruthenium benzoates, the authors were able to assign a pseudo-Hammett parameter of \( \sigma_{ortho} = 0.2 \), which was valid because the ortho substituents were sufficiently removed from the Ru\(_3\) core that the steric...
components were almost negligible. However, for the Mo₂PWCs herein, this is not the case, as shown from the aforementioned gas-phase calculations, so assigning a pseudo-Hammett constant in this case is not useful.

Compound 3c has only three formamidinate ligands, so with a reduction in steric bulk around the Mo₂ core, there is an increased likelihood that THF could coordinate axially. This additional electron density would make the Mo₂ core easier to oxidize and would manifest itself as an artificially low $E_{1/2}$ value for the complex. Therefore, the electrochemical data for 3c (and 2c for comparison purposes) were obtained in CH₂Cl₂. Pleasingly, the $E_{1/2}$ value for 2c in CH₂Cl₂ (338 mV) is very similar to that in THF (335 mV), which indicates that, in THF solutions, no THF is bound to the axial position of the paddlewheel complex. Considering the trend in the data for 2b–2i, this is likely the case for the whole series and therefore means that a reasonable comparison can be drawn between 3c

![Figure 6](image1.png) **Figure 6.** Calculated (PBE0/def2-TZVPP) frontier molecular orbitals and energy-level diagrams of 2c (left) and 3c (right) displayed with a course cube grid and an isovalue of 0.02. The HOMO and LUMO show mostly Mo₂-δ and Mo₂-δ* character, respectively.

![Figure 7](image2.png) **Figure 7.** Cyclic voltammetry data for each compound annotated with their fluorine substitution pattern. In all cases, the initial scan direction was from low to high potential.

![Figure 8](image3.png) **Figure 8.** Least-squares regression plot showing the relationship between the oxidation potential of compounds 2b–2g, 2i, and 3c and the corresponding Hammett constant. $R^2$ values were calculated without including data for 3c.

| compound | $E_{pa}$ | $E_{pc}$ | $\Delta E_p$ | $E_{1/2}$ | $i_{pa}/i_{pc}$ |
|----------|---------|---------|-------------|---------|-----------------|
| 2b       | 394     | 276     | 118         | 335     | 1.22            |
| 2c       | 238     | 149     | 89          | 194     | 1.16            |
| 2d       | 264     | 111     | 153         | 188     | 1.13            |
| 2e       | 157     | 66      | 91          | 111     | 1.08            |
| 2f       | 397     | 217     | 179         | 307     | 1.13            |
| 2g       | 316     | 173     | 143         | 225     | 1.16            |
| 2i       | 223     | 84      | 139         | 154     | 1.02            |
| 3c*      | 398     | 279     | 119         | 338     | 1.12            |

$^*$Data obtained in CH₂Cl₂.
and the homoleptic complexes 2x despite being in different solvents. As anticipated from analysis of the computational results, $E_{1/2}$ for 3c was lower than that for 2c (by ca. 18 mV), which is a consequence of fewer electron-withdrawing ligands around the core.

Evaluating the Air Stability. In order to test our hypothesis that strongly withdrawing ligands can lead to oxygen-tolerant Mo$_2$PWCs, we monitored the degradation of selected complexes upon exposure to atmospheric oxygen using NMR spectroscopy. Our focus was initially on two complexes at either end of the Hammett spectrum, namely, 2b (4-F) and 2j [3,5-(CF$_3$)$_2$], with the latter bearing the most electron-withdrawing substituents. To obtain a baseline spectrum for each compound (Figure 9, 0 h), the NMR spectra were recorded in a J. Young NMR tube under a nitrogen atmosphere using acetone-$d_6$, which had been previously freeze-pump-thaw-degassed and stored under nitrogen (no efforts were made to exclude moisture). For subsequent measurements, a separate solution was prepared (from the same batch of the sample) in air using a standard NMR tube and acetone-$d_6$ straight from the bottle. The timer was started upon dissolution of the complex.

In an aerated solution, 2b becomes light brown within a few minutes upon exposure to air. However, the NMR spectra illustrated that this considerable color change did not correspond to complete loss of the characteristic resonances. Even after 6 h, the resonances corresponding to 2b were still the dominant signals in the NMR spectra. In the first 9 min after the compound was exposed to air, the small secondary resonances (attributed to an axially coordinated Lewis adduct of 2b) disappeared from the $^1$H and $^{19}$F NMR spectra, and this was accompanied by a reduction in the intensity of the major product resonances. It is possible that this represents displacement of the axial ligand by the incoming oxygen and could hint toward an initial mechanistic step in the oxidative decomposition pathway. Alternatively, the Lewis adduct would be more electron-rich than the free complex and thus more easily oxidized and is likely consumed more quickly in the reaction. After 13 h, an opaque dark-brown solution had formed and very little 2b was observed in the NMR spectra. The decomposition of 2j was significantly slower and showed that, even after 23 h, a significant proportion of 2j remained in the sample, despite the solution turning from yellow to light brown. In the $^1$H NMR spectrum, the resonances associated with 2j were no longer the major peaks in the spectrum after 61 h, and by 144 h, the solution was dark brown and the resonances from 2j were no longer easily distinguished from the baseline. Unfortunately, we were unable to observe the decomposition products via MALDI-TOF MS, and this was also the case for all examples herein. The species formed upon decomposition is unknown, but there is no indication that the pathway involves a loss of ligand 1j because this has a characteristic formamidine (C−H) resonance at $\delta$H = 9.66, which does not appear at any point. To quantify the rate of decay for 2b versus 2j, we repeated these measurements with the inclusion of an internal standard of known concentration, 1,3,5-tris(trifluoromethyl)benzene (0.6 mmol dm$^{-3}$). The decay curves are displayed in Figures S109 and S111 and appear to show a first-order decay with rate constants [as determined from a plot of ln(2x) vs time] of 0.049 h$^{-1}$ for 2b.

Figure 9. (a) $^1$H and (b) $^{19}$F NMR spectra of 2b (top) and 2j (bottom) showing oxidative decomposition of the respective compounds over time. *Residual 1,2-dichlorobenzene.
and 0.021 h\(^{-1}\) for 2j, demonstrating a clear decrease in the rate of decay for the more electron-deficient Mo\(_2\) core of 2j.

Complex 2j shows an increased resistance to oxygen compared to 2b, which can be attributed to the increasingly withdrawing ligands, leading to an overall stabilization of the Mo\(_{10}\) core. However, homoleptic complexes such as 2b–2j are not overly useful in the construction of functional materials because the formamidinate ligand is kinetically inert. Conversely, heteroleptic compounds of the form Mo\(_2\)(NN)\(_2\)OAc are key starting materials for the construction of functionalized Mo\(_2\)PWCs because the OAc ligand is kinetically labile and can be substituted for a more functional ligand with ease.\(^{34,38}\) Unfortunately, this increased lability of the ligands is often accompanied by an increased sensitivity under atmospheric conditions. The most commonly employed formamidinate ligand in Mo\(_2\) chemistry is DAniF\(^{-}\), which features a methoxy functionality in the 4 position on the arene.\(^{34,41}\) While there are many advantages to this ligand (good solubility profile, good for growing crystals, etc.), Mo\(_2\)(DAniF)\(_2\)OAc remains quite air-sensitive. Curious to see if our strategies could increase the oxygen tolerance of Mo\(_2\)(NN)\(_2\)OAc-type complexes, 3c was subjected to similar NMR experiments and compared to Mo\(_2\)(DAniF)\(_2\)OAc. Ligand 1c was chosen specifically because the corresponding homoleptic complex (2c) yielded the highest measured oxidation potential in the series and thus is likely to represent the most stable option. As before, the NMR sample of 3c was prepared using benchtop acetone-\(d_6\) under ambient conditions (see the SI for NMR spectra). Unfortunately, decomposition was rapid, and no trace of the starting material was observed after 7.5 h (Figure S113). Dissociation of carboxylates from Mo\(_2\)PWCs is known to be solvent-dependent,\(^{38}\) and so the stability of 3c and Mo\(_2\)(DAniF)\(_2\)OAc in CDCl\(_3\) was also explored. In this case, decomposition took significantly longer, with significant quantities of 3c observable in the spectrum after 98 h in “oxygenated” CDCl\(_3\) (Figure S114), compared to complete decomposition of Mo\(_2\)(DAniF)\(_2\)OAc within 4 h. A quantitative analysis of this decomposition also described a first-order decay with rate constants of 0.016 h\(^{-1}\) for 3c, which is over an order-of-magnitude slower decay than that of Mo\(_2\)(DAniF)\(_2\)OAc (0.44 h\(^{-1}\); Figure S119). The stability of 3c in the solid state was also analyzed. A batch of solid, powdered 3c was exposed to ambient atmosphere and monitored over time. At regular intervals, a sample was taken and transferred to a Schlenk tube, and an NMR sample was prepared in acetone-\(d_6\) under oxygen-free conditions, thereby “quenching” the reaction of the solid material with oxygen. Over the course of 114 h, only a slight darkening of the color was observed in the exposed batch of 3c, and the final \(^1\)H NMR spectrum remained identical with the original (details are given in the SI). A second sample was left undisturbed for 170 h (Figure S120), and some darkening was observed. However, agitation of this sample at this point generated a much lighter-yellow powder, indicating that oxidation had only occurred on the exposed surface and that the bulk remained unoxidized. This was confirmed by NMR spectroscopy, which shows a seemingly unchanged spectrum even after 216 h. This is particularly remarkable because we observed powdered Mo\(_2\)(DAniF)\(_2\)(OAc), a well-known analogue of 3c, to darken to a deep-red color within 60 min upon exposure to air and to black within 24 h (Figure S122). Full decomposition of the bulk of Mo\(_2\)(DAniF)\(_2\)OAc was confirmed by \(^1\)H NMR spectroscopy (Figure S123).

## CONCLUSION

The exceptional redox and optical properties of Mo\(_2\)PWCs make them promising candidates for the development of functional materials; however, their sensitivity to oxygen is a severe roadblock toward that end. Herein, we have developed a family of homoleptic paddlewheel complexes derived from easily synthesized ligands with various fluorine substitution patterns. We have shown that the redox properties (\(E_{1/2}\)) of the subsequent Mo\(_2\)PWCs can be tuned predictably according to well-known Hammett parameters. Moreover, oxidation of the Mo\(_2\) core still occurs at easily accessible potentials that are relevant for application in functional materials. Studies into the oxidative decomposition of selected complexes by NMR spectroscopy showed an exceptional increase to the persistence (and a concomitant decrease of the observed decay constant) of complexes with higher \(E_{1/2}\) in the presence of atmospheric oxygen. Remarkably, an increased stability to oxygen was observed, even in heteroleptic complexes with kinetically labile acetate ligands. Notably, increasing the redox potential did not generate Mo\(_2\)PWCs which are indefinitely stable to oxygen, which implies that there is a strong kinetic component to the oxidative decomposition process, and overcoming this obstacle to air stability will be the subject of future studies. However, we have unambiguously demonstrated that, through judicious choice of a fluorination pattern on the ligands, Mo\(_2\)PWCs with remarkable tolerance to atmospheric oxygen can be accessed, which are particularly stable in the solid state. Furthermore, complexes with bespoke and functionally useful electrochemical properties can be designed and prepared with ease, paving the way for translating Mo\(_2\)PWCs into functional materials.

## EXPERIMENTAL SECTION

### Materials and Methods

All reagents were purchased from commercial sources and used without further purification. Anhydrous THF and hexane were obtained from an Innovative Technology Inc. PureSolv solvent purification system. Anhydrous 1,2-dichlorobenzene, CDCl\(_3\), CD \(_2\)Cl\(_2\), and deuterated dimethyl sulfoxide (DMSO-d\(_6\)) were obtained by drying over calcium hydride overnight before distillation. Anhydrous ethanol was obtained via distillation over magnesium and iodine. Acetone-\(d_6\) and 1,2-difluorobenzene (DFB) were deoxygenated under a three freeze–pump–thaw cycles under nitrogen. \(^1\)H, \(^13\)C, and \(^19\)F NMR spectra were recorded on a JEOL EGX400 or a JEOL ECS400 spectrometer, operating at 400 MHz for \(^1\)H, 100 MHz for \(^13\)C, and 376 MHz for \(^19\)F, or a Bruker AVIII300NB Ultrashield spectrometer, operating at 300 MHz for \(^1\)H and 282 MHz for \(^19\)F, respectively; all spectral data were acquired at 298 K. Chemical shifts (\(\delta\)) are quoted in parts per million (ppm). The residual solvent peaks (\(\delta\)) are used as references. Coupling constants (\(J\)) are reported in hertz to the nearest 0.1 Hz. The multiplicity abbreviations used were as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad singlet. Mass spectra (low and high resolution) were obtained by the University of York Mass Spectrometry Service, using electrospray ionization (see the SI) on a Bruker Daltonics Micro-TOF spectrometer or a solarix XR FTMS MALDI-TOF spectrometer using dithranol as the matrix in each case. Dithranol was obtained from commercial sources and used as received. CHN elemental microanalysis was performed by Graeme McAllister at the University of York using an Exeter Analytical Inc. CE-440 analyzer. UV/visible absorption spectra were recorded on a Jasco Y-560 UV/visible spectrophotometer using an airight quartz cuvette fitted with a J. Young trap. Cyclic voltammetry experiments were recorded on a Gamry reference 600 (Gamry Instruments, Warminster, PA) under an
atmosphere of dry argon in a solution of THF with 0.1 M \( \text{Na}_{2}\text{Bu}_{4}\text{PF}_6 \). A standard three-electrode setup was employed and consisted of a 3 mm platinum disk working electrode and two separate platinum wires for the reference and auxiliary electrodes. All potentials were referenced to the \( \text{Fc/Fe}^+ \) redox couple and corrected for a pseudopotential drift and cell resistance using values obtained from impedance measurements. Single-crystal XRD data were collected on a single source from two available sources (Cu \( \text{K} \alpha \) radiation, \( \lambda = 1.54184 \ \text{A} \); Mo \( \text{K} \alpha \) radiation, \( \lambda = 0.71073 \ \text{A} \)) with an Oxford Diffraction SuperNova X-ray diffractometer. Crystals were cooled to 110 K with an Oxford Instruments Cryojet. The data were collected and refined by Adrián Whitwood and Theo Tanner, University of York. A redetermination of compounds 2b, 2j, 3c, and \( \text{MeO}_2(\text{DAniF})_2(\text{OAc}) \) was followed by time-course measurements of the \( \text{H}^+ \) and \( ^{19} \text{F} \) NMR spectra where appropriate. A quantitative measurement of the decomposition of each species was obtained through a comparison to an inert, nonvolatile internal standard of known concentration [1,3,5-tris(trifluoromethyl)benzene, 1.07 \times 10^{-2} \text{ mol dm}^{-3}]. More specific details of the calculations can be found in the SI and Tables S1–S7.

**Synthesis**. The formamidinate ligands, where \( R = \text{Ph} \) (1a), -4-F (1b), 3,5-F\(_2\) (1c), 2,3,5-F\(_3\) (1d), 3,4,5-F\(_3\) (1g), 4-Cl (1h), 3,5-Cl\(_2\) (1i), and 3,5-Cl\(_2\) (1j), were previously reported.

**General Procedure for the Synthesis of Formamidine Ligands (1a–1j)**. In a round-bottom flask, triethylorthofor- mate and the corresponding aniline were combined in a molar ratio of 1:2. The reaction mixture was heated to 140 °C for ca. 6 h before it was allowed to cool to room temperature. The crude product was recrystallized from toluene or a toluene/petroleum ether mixture, and the solids were washed with petroleum ether. Recrystallization was repeated until a colorless microcrystalline solid was obtained or until the product was analytically pure by \( \text{H}^+ \) NMR spectroscopy and CHN microanalysis. Crystals suitable for XRD were grown either from recrystallization from a mixture of toluene/hexane (2:1) or by the slow diffusion of hexane into a toluene solution of the compound.

**Notas**: The reaction rate can be enhanced with the addition of an acid catalyst. However, care must be taken because this can lead to the formation of colored salts, which can be difficult to remove via standard purification. For this reason, a catalyst (p-toluenesulfonic acid, ca. 2 mg) was used only when noncatalytic conditions proved to be stubborn.

**\( \text{N}^\text{N} \)-\( \text{Bi}(4-\text{fluorophenyl})\text{formamidine} (1b)**. Triethylorthofor- mate (2.3 ml, 14 mmol), 4-fluoroaniline (2.7 ml, 28 mmol), and p-toluenesulfonic acid were used. A colorless microcrystalline solid was obtained. Yield: 65.6% (2.15 g, 9.26 mmol).

**\( \text{N}^\text{N} \)-\( \text{Bi}(3,5-\text{difluorophenyl})\text{formamidine} (1d)**. Triethylorthofor- mate (2.3 ml, 14 mmol) and 3,5-difluoroaniline (3.07 g, 28.2 mmol) were used. Yield: 82.2% (3.11 g, 11.6 mmol).

**\( \text{N}^\text{N} \)-\( \text{Bi}(3,5-\text{dilfluorophenyl})\text{formamidine} (1e)**. Triethylorthofor- mate (2.3 ml, 14 mmol) and 3,5-difluoroaniline (3.07 g, 28.2 mmol) were used. Yield: 82.2% (3.11 g, 11.6 mmol).

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and decanting off the solution via a filter cannula. The solids were washed with ethanol a further two-to-three times to give a yellow powder. Yield: 9.2% (0.14 g, 0.47 mmol).

\[ \text{Calcd for C}_{15}H_{28}F_{2}Mo_{2}N: m/z 1120.10 ([M]^{+}) \]

Single crystals were grown by slow diffusion of hexane into a THF solution of 2f.

**Dimolybdenum Tetrakis[N,N'-bis(3,4-trifluorophenyl)formamidinate]** (2g). Molybdenum hexacarbonyl (0.26 g, 0.42 mmol) and 1h (2.00 g, 3.19 mmol) were used. The solution was heated for 21 h. Yield: 19.6% (0.26 g, 0.16 mmol). \(^1\)H NMR (400 MHz, CDCl3): \(\delta = 8.67 \text{ (s, 4H, NC(H)N), 6.58 (br, 16H, o-C-H)}. \)

**Quantum-Chemical Calculations.** All calculations were performed using the Gaussian 16, revision A03, package. NBO analysis was performed using the NBO 7.0 package. The initial geometry was refined using the B3LYP functional with the 6-31G(d) basis set.
optimization calculations were performed at the B3LYP/def2_SV(P) level, followed by frequency calculations at the same level. Local minima were identified by the absence of imaginary frequency vibrations. In the (RI-)BP86/def2_SV(P) calculations, a 60-electron quasi-relativistic effective core potential replaced the core electrons of molybdenum. No symmetry constraints were applied during optimizations. Single-point calculations (performed using the Gaussian 16, revision A.03, package) on the B3LYP/def2_SV(P)-optimized geometries were performed using the hybrid PBE0 functional and the flexible def2_TZVPP basis set. TD-DFT calculations were performed using the hybrid PBE0 functional and flexible def2_TZVPP basis set using input geometries optimized at the B3LYP/def2_SV(P) level. The first 10 excitations were performed. These calculations were undertaken on the Viking Cluster, which is a high-performance computer facility provided by the University of York.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02746.

Calculated coordinates (XYZ)

Experimental procedures, spectra, crystallographic tables, and quantum-chemical calculations (PDF)

Accession Codes
CCDC 2193729, 2193736, 2193737, 2193739, 2193741, 2193742, 2193744–2193747, 2193749, 2193752, and 2193937 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
L.A.W. is grateful to the Leverhulme Trust for his Early Career Fellowship (ECF-2019-134) and for the RSC Enablement Grant E21-393944046. B.C.T. is grateful to the University of York for his studentship. We are grateful for computational support from the University of York High Performance Computing Service, Viking Cluster, and the Research Computing team. Prof. Jason Lynam and Dr. John Slattery are gratefully acknowledged for advice and helpful discussion with computational chemistry.

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