Redox Tuning of the Dimolybdenum Compounds at the Ligand Periphery: A Direct Correlation with the Hammett Constant of the Substituents

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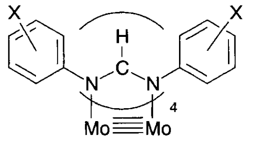
Oxidation potentials of [$Mo_2(ArNCHNAr)_4$] (Ar = aryl), a direct measure of the HOMO (δ orbital) energy, correlate with the Hammett constant of aryl substituents, while both structural and spectroscopic data indicate that the valence structure around the dinuclear core is unperturbed.

Ligand control over the redox properties of transition-metal complexes is a central theme in homogeneous catalysis,[1] electron-transfer reactions,[2] and charge-transfer based materials.[3] Such control depends on the nature of the coordinating atoms, the steric factors about the metal centre, and the substituent effects away from the first coordination sphere. The latter, while less dramatic than the first two factors, is often desired since it invokes minimum change in coordination geometry, and often has no effect on the *distribution* of metal-based valence orbitals. This effect on metalloporphyrins has been extensively studied,[4] and proven to be instrumental in improving the stability of the compounds which mimic cyt-P_{450} in the oxygenation of hydrocarbons.[5] Studies of ruthenium–polypyridyl systems also demonstrated that substituent effects can be critical in optimizing the photophysical properties of the well-known MLCT excited state.[6] As part of our effort to explore both the general reactivity and the catalytic properties of dinuclear transition-metal compounds containing a metal–metal bond, we report herein the first example of substituent redox-tuning of the quadruply bonded dinuclear species,[7] namely tetrakis(diarylformamidinato)dimolybdenum(II).



Analogously to tetrakis[di(*p*-tolyl)formamidinato]dimolybdenum **1**,[8] the dimolybdenum compounds were obtained as air-stable yellow crystalline materials by treating either $Mo(CO)_6$ or $Mo_2(OAc)_4$ with diarylformamidines[9] (aryl = XC_6H_4, X = *p*-OMe **2**, H **3**, *m*-OMe **4**, *p*-Cl **5**, *m*-Cl **6**, *m*-CF_3 **7**, *p*-COMe **8**, *p*-CF_3 **9**; or 3,5-$Cl_2C_6H_3$ **10**). Substituents were chosen to span a wide range in Hammett constants,[10] from −0.27 (*p*-OMe) to 0.74 (3,5-Cl_2).† X-Ray diffraction studies‡ of compounds **2** and **6** reveal that both molecules adopt the paddle-wheel structure and have Mo–Mo bond lengths of 2.0964(5) and 2.0958(6) Å, respectively, which are close to that of **1** (2.085 Å),[8] and typical for the quadruply bonded species.[11] Existence of the quadruple bond is further supported by the observed eclipsed geometry around the Mo_2 core (torsional angles N–Mo–Mo′–N′ are < 1° in both cases). The average Mo–N distances (2.158 Å for **2** and 2.161 Å for **6**) are also very similar to that of **1** (2.17 Å),[8] indicating that the Mo–N covalent bond is unperturbed by the inductive effect of the remote substituents.

Although structural details for the other members of the series are not available yet, they are assumed to be isostructural to those determined, since a D_4 or C_{4h} molecular symmetry is indicated by the ^1H NMR spectra of **2**–**10**.§ In addition to the Mo–Mo bond length, the magnetic anisotropy due to the ring current effect also serves as a sensitive probe of the bond multiplicity. Early work[12] indicated that the magnetic anisotropy can be accurately determined from the chemical shift of the methine proton (–NC*H*N–) of the bridging formamidinate based on the McConnell equation[13] [eqn. (1)]:

$$\Delta\chi = \Delta\delta/[(1 - 3\cos^2\theta)/12\pi r^3] \qquad (1)$$

where Δδ = δ(–NCHN– in Mo_2) − δ(–NCHN– in Ni_2),¶ and *r* is the estimated distance between the methine proton and the centroid of Mo–Mo vector. Table 1 shows that Δχ across the series varies in a narrow range, and the variance is unrelated to the Hammett constant of the substituents. Thus the accumulation of the bonding electron density along the Mo–Mo vector is essentially a *constant*, reinforcing our belief that the Mo–Mo quadruple bond is not affected by the remote substituent. Electrochemical study of compounds **2**–**9** showed that they all undergo a (quasi)reversible oxidation [eqn. (2)].

$$[Mo_2L_4] \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [Mo_2L_4]^+ \qquad (2)$$

This oxidation can be attributed to the removal of an electron from the Mo–Mo δ-bonding orbital,[8] and its half-wave potential ($E_{1/2}$, determined from cyclic voltammetry *vs.* Ag–AgCl reference electrode) thus provides a reliable measure of the *E*(HOMO). The measured $E_{1/2}$ values range from +244 mV for **2** to +795 mV for **9**, and are shifted anodically as the electron withdrawing ability of the substituent increases. Furthermore, a linear least-squares fitting of the $E_{1/2}$ − 8σ plot|| (Fig. 1) revealed a Hammett equation [eqn. (3)][14] with a correlation coefficient of 0.993 and ρ = 87.2 mV.

$$E_{1/2}(Mo_2^{5+}\text{–}Mo_2^{4+}) = 428\ \text{mV} + 8\sigma\rho \qquad (3)$$

Table 1 Experimental results for [$Mo_2(ArNCHNAr)_4$]

X	*p*-OMe	*p*-Me[a]	H	*m*-OMe	*p*-Cl	*m*-Cl	*m*-CF_3	*p*-COMe	*p*-CF_3	3,5-Cl_2
σ	−0.27	−0.17	0	0.12	0.23	0.37	0.43	0.50	0.54	0.74
$E_{1/2}$[b]/mV	244	333	418	458	601	683	762	778	795	[c]
(ΔE_p/mV, i_{pc}/i_{pa})	(158, 0.98)	(191, 0.97)	(93, 0.96)	(197, 1.01)	(250, 1.19)	(177, 0.99)	(155, 0.75)	(137, 0.73)	(155, 0.77)	
δ (–NC*H*N–)	8.38	8.45	8.53	8.58	8.43	8.53	8.62	8.71	8.62	8.54
Δχ(10^{-36} m^3 $molecule^{-1}$)	4950	5060	5000	5040	4900	4890	4820	—	—	4730
λ_{max} (δ–δ*)[d]/nm	430	438	440	442	438	442	442	436	446	444
λ_{max} (others)[d]/nm	274, 288, 310, 384	270, 290, 316, 375	270, 288, 312, 370	280, 294, 318, 384	270, 294, 320, 384	270, 290, 312, 384	272, 288, 308, 384	308, 336,	268, 296, 314, 386	272, 292, 320, 382

[a] Spectroscopic and electrochemical data for this compound were reported in ref. 8, but were re-determined here to ensure a consistent experimental condition across the series. Only minor deviation was noticed. [b] Measurement was carried out in CH_2Cl_2 with Bu_4NBF_4 as the supporting electrolyte, Pt working and auxiliary electrodes, Ag–AgCl reference electrode, [Mo_2] ≈ 1 mmol dm^{-3}, and scan rate of 100 mV s^{-1}; Under these conditions, the $E_{1/2}(Fc^+\text{–}Fc)$ was consistently measured at +625 mV. $E_{1/2} = (E_{pa} + E_{pc})/2$ and $\Delta E_p = E_{pa} - E_{pc}$. [c] Irreversible. [d] UV–VIS spectra were recorded in degassed CH_2Cl_2.

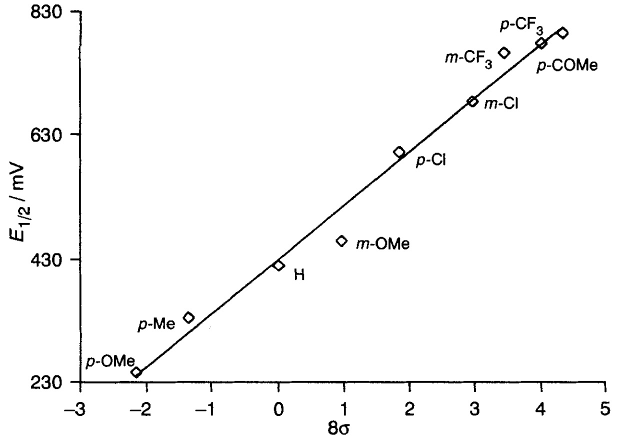


Fig. 1 Dependence of $E_{1/2}$ on the Hammett constant σ: the diamonds are the measured values, and the solid line is the least-squares fit

The 3,5-dichloro compound (**10**, σ = 0.74) should undergo a reversible oxidation with an $E_{1/2}$ of 944 mV according to eqn. (3). Instead, only an anodic peak was observed at 1029 mV, indicating that the dimolybdenum core becomes very electron deficient. These results thus clearly demonstrate that the HOMO energy of the dinuclear core can be effectively controlled with appropriate aryl substitution. Consistent with the measured $E_{1/2}$, compound **2** dissolved in dry CH_2Cl_2 turned brown within minutes when exposed to air, while the solution of **10** displayed identical UV–VIS spectra even after being exposed to air for a week.

Interestingly, compounds **1–10** exhibit very similar UV–VIS spectra (see Table 1). In particular, the δ–δ* (HOMO–LUMO) transitions consistently appear in the narrow range 430–446 nm (2.78–2.88 eV), revealing that the substituent effect on the δ* orbital must be approximately equal to that on the δ orbital. For all the compounds except **8**, four other observed transitions attributed to the dipole-allowed LMCT[8] [N–δ*(Mo–Mo) and N–π*(Mo–Mo) transitions] occurred at similar λ_{max}. It can thus be inferred from this spectral similarity that both the *relative* distribution and the composition of the upper valence orbitals of dimolybdenum compounds are *not* influenced by remote substituents.

In conclusion, we have succeeded in utilizing the remote substituents to control the redox potential of a dimolybdenum(II) compound while preserving its valence structure. We are currently exploring the possibility of using this effect to improve the resistance towards oxidative degradation of certain diruthenium(II) complexes, which may function as olefin metathesis catalysts.[15]

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Footnotes

[†] Assuming that the additivity of Hammett constants holds; see ref. 10.

[‡] *Crystal data* for **2**: pale yellow crystal from hexane–CH_2Cl_2, $C_{60}H_{60}Mo_2N_8O_8$, M = 1213.0, triclinic, space group $P\bar{1}$, a = 10.314(1), b = 10.405(1), c = 13.996(1) Å, α = 80.65(1), β = 75.76(1), γ = 81.55(1)°, U = 1427.4(3) Å^3, Z = 1, D_c = 1.411 g cm^{-3}, μ = 0.500 mm^{-1}, absorption corrections (ψ) were applied; $R1$ = 0.0395, $wR2$ = 0.113, and goodness of fit = 1.427 for 4989 unique observed data and 407 parameters.

Crystal data for **6**: pale yellow crystal from hexane–CH_2Cl_2, $C_{52}H_{36}Cl_8Mo_2N_8$, M = 1248.4, triclinic, space group $P\bar{1}$, a = 9.962(3), b = 11.555(3), c = 12.463(3) Å, α = 87.80(3), β = 75.90(3), γ = 65.85(2)°, U = 1266.6(5) Å^3, Z = 1, D_c = 1.637, μ = 0.963 mm^{-1}, absorption corrections (ψ) were applied; $R1$ = 0.0310, $wR2$ = 0.0903 and goodness of fit 1.281 for 4455 unique observed data and 371 parameters.

Data sets were collected on a Siemens P4 diffractometer (Mo-Kα radiation, λ = 0.71073 Å, θ–2θ mode, θ range 2.0–25.0°) at 293 K. Solutions and refinements (full-matrix least squares on F^2) were performed using SHELXTL PLUS, PC Version 5.01β. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were located and refined with B_{eq} = 1.2 times attached carbon atoms, except for the methoxy protons of **2**, which were disordered and idealized atoms were generated and refined with B_{eq} = 0.08.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[§] *^{1}H NMR data* for compounds **2–10**, δ($CDCl_3$): **2**, 6.51 (16 H), 6.17 (16 H), 3.71 (24 H); **3**, 6.93 (24 H), 6.22 (16 H); **4**, 6.89 (8 H), 6.48 (8 H), 6.07 (8 H), 5.84 (8 H); **5**, 6.97 (16 H), 6.13 (16 H); **6**, 6.97 (16 H), 6.17 (16 H); **7**, 7.25 (8 H), 7.14 (8 H), 6.57 (8 H), 6.29 (8 H); **8**, 7.58 (16 H), 6.31 (16 H), 2.51 (24 H); **9**, 7.25 (16 H), 6.27 (16 H); **10**, 7.08 (8 H), 6.11 (16 H). The chemical shifts of the methine protons are given in Table 1.

[¶] See ref. 12 for more discussion. $Ni_2(ArNCHNAr)_4$ corresponding to **2–6**, **9** and **10** have been synthesized (unpublished work). δ(–NC*H*N–) ($CDCl_3$): 6.15(*p*-OMe), 6.17(*p*-Me), 6.28(H), 6.31(*m*-OMe), 6.22(*p*-Cl), 6.33(*m*-Cl), 6.45(*m*-CF_3), 6.41(3,5-Cl_2).

[||] There are eight aryl groups per molecule.

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