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'Electronic bending' of imido ligands and the effect on the coordination mode of a tridentate ancillary ligand

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Abstract

The five-coordinate mixed-imido complex $[Mo(Nt-Bu)(NC_6F_5)(L)]$ (1) can be prepared in high yield via treatment of $[Mo(Nt-Bu)(NC_6F_5)(Ot-Bu)_2]$ with LH₂, where LH₂ is 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine. Contrastingly, the reaction of $[Mo(N-Ad)(NC_6F_5)(Ot-Bu)_2]$ (Ad = adamantyl, C_6H_{10}) with LH₂ gave $[Mo(NAd)_2(L)]$ (2) via an imido-exchange reaction. Complex 2 can also be synthesised via treatment of in situ generated $[Mo(NAd)_2(Ot-Bu)_2]$ with LH₂; the latter method also results in trace amounts of the five-coordinate complex $[MoCl(NAd)_2(L_{dehyd})]$ (3) $(L_{dehyd} = 2-(2-hydroxy-2,2-diphenylethenyl)pyridine)$. The structures of 1–3 have been determined by X-ray crystallographic study. In each complex, the geometry at the metal is distorted trigonal bipyramidal with the pyridinediolate ligand adopting an 'aea' bonding arrangement in 1 and an 'eee' arrangement in 2. The angle associated with the imido moiety also varies, with the greatest deviations found in 1 and 3, indeed, the pentafluoroimido ligand in 1 has one of the largest deviations from linearity for an M–N–C angle recorded to-date [135.98(16)°]. This has been rationalised on the basis of an electronic effect rather than intramolecular steric interactions or crystal packing forces.

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1. Introduction

The organoimido function has featured heavily in coordination chemistry over the last three decades [1]. Interest in bis(imido) complexes of group VI in-particular continues, primarily because of their use as precursors to useful catalytic systems [2]. The vast majority of terminal organoimido (NR, R = alkyl or aryl) groups in the literature are sp-hybridised at nitrogen and hence triple-bond in nature (four electron donors). The softness of the M–N–C angle has been noted previously with angles in the range 180–150° considered linear (I) [3]. An additional linear form (II) with a formal M = N double bond has also been

noted [4]. Contrastingly, there are few examples of bent imido groups (III), although a number of chelate species are known where the restricted imido bond angle is a function of the bite angle of the ligand [5]. In the case of III, the lone pair resides on the sp²-hybridised nitrogen atom and the metal imido group can be described as possessing double-bond character (2 electron donor).



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The earliest structurally characterised example [Mo- $(NPh)_2(S_2CNEt_2)_2]$, a 20 electron complex, was found to possess one bent $[Mo-N-C = 139.4(4)^{\circ}]$ and one linear $[Mo-N-C = 169.4(4)^{\circ}]$ imido group at $-80 \,^{\circ}C$ [6]; only slight differences were observed in a later room temperature study [7]. Interestingly, the related complexes [Mo- $(NAr)_{2}(S_{2}CNEt_{2})_{2}]$ (Ar = 2-MeC₆H₄, 2,6-Me₂C₆H₃, 2,6-*i*- $Pr_2C_6H_3$ and 2,6- $Cl_2C_6H_3$) do not contain bent imido groups, leading to the conclusion that the bending of the imido ligand in this system is attributable to intramolecular steric interactions and/or crystal packing forces [7]. Examples of bent imido ligands for other metals (see Table 1) include the manganese complexes $[Mn(Nt-Bu)_3X]$ $(X = Cl, OC(O)Me, OC_6F_5 \text{ and } SC_6F_5)$ for which the Mn–N–C angles fall in the range $138.5(3)-144.6(3)^{\circ}$ [8], and the rhenium(VII) complex $\{[Re(Nt-Bu)_2(\eta^1 C_{5}H_{5}]_{2}(\mu - C_{5}H_{4})(\mu - O)\}$ [9]. Recently, Odom et al. have carried out a statistical analysis of bis(imido) group VI complexes using data from the Cambridge Structural Data Base, and presented the data in terms of the sum of the imido angles [10]. The average sum of the imido angles was found to be 328° (standard deviation 8°), whilst it was also apparent that bending of the imido group was no more prevalent for 6-coordinate complexes than for 4or 5-coordinate species.

In our previous studies on the 2,6-bis(2-hydroxy-2,2diphenylethyl)pyridine (LH₂), IV, we have described the synthesis and X-ray crystal structure of the five-coordinate molybdenum (VI) compound [Mo(NAr)₂(L)], where $Ar = N-2.6-i-Pr_2C_6H_3$ [3]. In this case the pyridinediolate ligand adopts a 'facial', (eae) coordination mode¹ leaving one of the imido ligands to occupy an axial coordination site within the trigonal bipyramidal structure, the other imido group occupies an equatorial site. The structure of this complex revealed a severe bending of the equatorial imido ligand, $[144.8(5)^{\circ}]$ the axial imido group remaining essentially linear [164.7(4)°]. In order to help understand whether the bending was due to an electronic or steric effect, the related alkylidene complex was prepared and structurally characterised. Here, the alkylidene ligand was found to preferentially occupy the equatorial site and is of course necessarily bent due to the sp²-hybridised alkylidene carbon centre. Indeed, it was thought likely that the alkylidene ligand would prefer the equatorial site since in that position there exists only one $d\pi$ metal orbital available for bonding to the π -ligand. Thus, the bending of the imido group in this environment may be attributed to an electronic explanation rather than due to steric effects or crystal packing forces. In extending this work, we wished to probe the effect of incorporating differing imido ligands, especially those with different electronic requirements, i.e. an electron-withdrawing substituent and electron-releasing substituent within an this

¹ We have opted not to use the terms *fac* and *mer* here, as IUPAC usually reserves such descriptions for hexa-coordinate centres.

5-coordination geometry. Furthermore, would an imido ligand with a strong electron-withdrawing substituent show a preference for the equatorial site. We were also interested to compare the effect of *facial* (eae) coordination of the [O,N,O] ligand with *meridional* (eee) coordination, and the effect this might have on the imido ligand bonding.

Table 1 Bent imido groups

Compound	M–N–C angle (°)	Metal coordination number	Reference
$[CrO(Nt-Bu)(O(Ph_2SiO)_2)_2]$	145.6(6)	4	[11]
	146.4(6)		
$[Cr(NAr)(O)(Ni-Pr_2)(Ar)]$	146.2(3)	4	[12]
$[Cr(O)(NSiMe_2)(pv)]_{2}$ -	144.1(3)	5	[13]
$(u-OSiMe_2)$			[]
$[Mo(NPh)_2(S_2CNEt_2)_2]$	139.4(4)	6	[6.7]
	[141.4(5)]		L - 2 - 3
	169.4(4)		
	[170 9(6)]		
[Mo(NAr) ₂ L]	144 8(5)	5	[3]
	1647(4)	5	[5]
$[M_0(N_t-B_u)(N_C \in F_t)L]$	135 98(16)	5	this work
	173 52(18)	5	this work
[Mo(NAd) ₂ C](LH ₄₋₁ ,,)]	148.6(3)	5	this work
[into(intra)2en(Erridenya)]	170.9(3)	5	this work
$[Mn(Nt-Bu)_{2}C1]$	1385(3)	4	[8]
	141.8(3)	7	[0]
	141.6(3) 140.6(3)		
$[Mn(Nt-Bu)_{2}(OC(O)Me)]$	140.0(3) 144 6(3)	4	[8]
	140.1(5)	7	[0]
	140.1(5) 142.2(5)		
$[Mn(Nt-Bu), (OC-E_{-})]$	142.2(3) 141 9(2)	4	[8]
	130.0(2)	7	[0]
	139.9(2) 140.7(2)		
$[M_{P}(N_{t}, \mathbf{B}_{H}) (N_{t}, \mathbf{H}, t, \mathbf{B}_{H})] (\mathbf{PE})^{a}$	140.7(2) 141.0(6)	4	[8]
	141.0(0) 141.4(6)	7	[0]
	141.4(0) 146.5(6)		
[Mn(Nt Bu), (NH, t)]	135.8(6)	4	[8]
$\mathbf{P}_{11} = \mathbf{P}_{11} = \mathbf{P}$	133.8(0) 140.5(7)	4	[0]
Bu)](03SCI'3)	140.3(7) 126 2(4)		
$[M_{P}(N_{t}, \mathbf{D}_{N}) (\mathbf{S}_{t}, \mathbf{E}_{t})]$	130.2(4) 142.1(2)	4	101
[WIII(INI-Bu)3(3C61'5)]	143.1(2) 142.0(2)	4	႞၀႞
	142.0(2) 142.2(2)		
$\left[\left[\mathbf{P}_{\mathbf{a}}(\mathbf{N}_{t},\mathbf{P}_{\mathbf{u}})\right]\left(\mathbf{n}_{t}^{1},\mathbf{C},\mathbf{H}_{t}\right)\right]$	142.2(2) 146.1(10)	5	[10]
$\{[\mathbf{Ke}(\mathbf{N}_{i}-\mathbf{Bu})_{2}(1_{i}-\mathbf{C}_{5}1_{5})]_{2}^{2}$	140.1(10) 152.5(12)	5	
$(\mu - C_{5} \Gamma_{4})(\mu - O)$	152.3(12) 172.4(11)		
	1/5.4(11) 176.2(12)		
[D ₂ (N ₁ t D ₁) (magitul)]	1/0.2(12) 1/0.2(12)	4	[14]
$\mathbf{M}_{2}\mathbf{C}]$	142.4(22)	4	[14]
$\begin{bmatrix} \text{NIOCI}(\text{N}t-\text{Bu})_2(\text{O}-\text{O}) \end{bmatrix}$	146.57	3	[15]
$[\text{Re}(\text{IN}t-\text{Du})_3(\text{IN}\Pi_2t-\text{Du})]^-$	140.0(8) 120.8(7) ⁶	4	[10]
(SU_3CF_3)	139.6(7)	5	[17]
$[\text{Re}_4(\text{N}t\text{-Bu})_8(\mu\text{-O})_2(\mu_3\text{-O})_2\text{-} (\text{O}_3\text{SCF}_3)_4]$	143.9(6)	3	[1/]
$[Os(p-NC_6H_4NO_2)_2(TTP)]^d$	144.74	6	[18]
	141.91		
$[Os(p-NC_6H_4NO_2)_2-$	143.8(6)	6	[19]
(4-Cl-TTP) ^d	141.3(6)		

^a Severe disorder prevented an accurate structure determination.

^b (O-O) = ring-opened biaryl lactone.

^c Thought to be protonated.

^d TTP = tetratolylporphyrin.

In this paper, we report the successful synthesis and structural characterisation of two complexes $[Mo(Nt-Bu)(NC_6F_5)(L)]$ (1) and $[Mo(NAd)_2(L)]$ (2), which possess the desired *facial* and *meridional* coordination geometries, respectively. The structure of the trace product $[MoCl(-NAd)_2(L_{dehvd})]$ (3) is also reported.

Few other studies of the tridentate ligand L have been reported, examples include oxo, nitrido and imido complexes of osmium [20], the dioxo complexes of molybdenum reported by Holm [21], a titanium dichloride complex [TiCl₂L] [22] and the main-group complex [SiMe₂L] [23–25]. We have also recently reported the isodiazene complex [MoCl(O₃SCF₃)(NNPh₂)L] which contains a *meridional* ligand [26].





Fig. 1. The molecular structure of 1 with H-atoms omitted.

Table 2 Selected bond lengths (Å) and angles (°) for 1

Mo(1)–N(1) 1.7228(19)	Mo(1)-N(2) 1.8074(19)
Mo(1)-O(1) 1.9173(15)	Mo(1)-O(2) 1.9274(15)
Mo(1)-N(3) 2.3914(18)	
N(1)–Mo(1)–N(2) 103.55(9)	N(1)-Mo(1)-O(1) 95.40(8)
N(2)-Mo(1)-O(1) 116.97(8)	N(1)-Mo(1)-O(2) 93.86(8)
N(2)-Mo(1)-O(2) 115.49(8)	O(1)–Mo(1)–O(2) 122.51(7)
Mo(1)-N(1)-C(1) 173.52(18)	Mo(1)-N(2)-C(5) 135.98(16)

2. Results and discussion

Starting materials of the form $[Mo(NR')(NR'')Cl_2(dme)]$ (R' = t-Bu, R'' = C₆F₅; R' = Ad, R'' = C₆F₅) have been used previously for the synthesis of mixed-imido compounds [27]. The five-coordinate complex $[Mo(Nt-Bu)(NC_6F_5)(L)]$ (1) can be prepared in multigram quantities via treatment of $[Mo(Nt-Bu)(NC_6F_5)(Ot-Bu)_2]$ (prepared in situ from $[Mo(Nt-Bu)(NC_6F_5)_2Cl_2(dme)]$ and LiOt-Bu) with LH₂.

Crystals of **1** suitable for an X-ray determination were grown from a saturated MeCN solution upon standing at room temperature. The molecular structure is shown in Fig. 1 and key bond lengths and angles are given in Table 2, crystal data are given in Table 3. The molecular structure is best described as a distorted trigonal pyramid with the pyridine of the diolate and the *tert*-butylimido groups occupying axial sites, i.e. an 'aea' set.

The 'aea' arrangement of the pyridinediolate (L) is similar to that observed in $[Mo(NAr)_2L]$ (Ar = N-2,6-*i*-Pr₂C₆H₃)² and [OsNCl(L)] [20]. The structural parameters associated with the two imido groups in **1** reflect their differing electronic properties. The result is one linear *tert*-butylimido ligand [Mo(1)-N(1) = 1.7228(19) Å, $Mo(1)-N(1)-C(1) = 173.52(18)^{\circ}]$ and one bent pentafluor-ophenylimido group [Mo(1)-N(2) = 1.8074(19) Å, $Mo(1)-N(2)-C(5) = 135.98(16)^{\circ}]$; a feature attributed to the more electron-releasing nature of the *tert*-butylimido ligand. In the bent ligand, there is also a diminished metal-nitrogen π contribution due to the presence of π -bonding between

the nitrogen and the *ipso*-carbon of the phenyl ring as evidenced by the short C(5)-N(2) distance [1.379(3) Å cf. 1.449(3) Å for C(1)-N(1)]. Table 1 contains literature examples of 'bent' imido groups and reveals that for complex 1 the imido group has one of the greatest deviations from linearity observed to-date. The sum of the imido angles for $1 = \text{ca. } 309.5(^\circ)$, which is very close to that observed for $[Mo(NPh)_2(S_2CNEt_2)_2]$ [309°] – which is the lowest 'sum' in the literature.

The five-coordinate complex $[Mo(NAd)_2(L)](2)$ can be prepared via treatment of $[Mo(NAd)(NC_6F_5)(Ot-Bu)_2]$ (prepared in situ from [Mo(NAd)(NC₆F₅)Cl₂(dme)] and LiOt-Bu) with LH_2 in refluxing toluene. The production of complex 2 at elevated temperatures indicates that under these conditions imido-ligand exchange occurs. Similar imido ligand exchange has been observed for the four-coordinate complexes $[MoX_2(Ot-Bu)_2]$ (X = O or NR), the tetratungstate [W₄(Nt-Bu)₄O₄Cl₁₀]²⁻ and more recently for the *tert*-butylimido titanium complex $[Ti(Nt-Bu)Cl_2(py)_2]$ [28–30]. It is also noteworthy that the bis(imido) complexes $2,6-C_6H_3-i-Pr_2$ $[Mo(NR)_2Cl_2(dme)]$ (R = t-Bu, and $[Mo(NAr)_2(Ot-Bu)_2]$ undergo metathesis with the imines PhN = CH(t-Bu) or (n-Pr)N = CHPh [31]. Crystals of $2 \cdot MeCN$ suitable for an X-ray determination were obtained from a saturated MeCN solution upon prolonged standing at ambient temperature. The molecular structure is shown in Fig. 2a and b; key bond lengths and angles

Table 3

Summary of crystal data and structure determination for compounds 1, 2 · MeCN and 3

Compound	1	$2 \cdot MeCN$	3
Formula	C43H36F5N3O2Mo	$C_{53}H_{57}N_3O_2Mo \cdot C_2H_3N$	C53H56ClN3OM0
M	817.69	905.01	882.40
Temperature (K)	160	160	160
Crystal size (mm)	$0.42 \times 0.17 \times 0.11$	$0.29 \times 0.23 \times 0.23$	$0.25 \times 0.18 \times 0.16$
Crystal colour, habit	yellow, block	yellow, block	yellow, block
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_{1}/c$	$P2_1/c$
a (Å)	11.0769(5)	25.762(11)	12.4861(12)
b (Å)	33.8115(16)	8.671(4)	18.1988(17)
c (Å)	11.2651(5)	21.877(11)	19.0842(18)
β (°)	116.687(2)	111.99(2)	99.806(2)
$V(\text{\AA}^3)$	3769.6(3)	4531(4)	4273.2(7)
Z	4	4	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.441	1.327	1.372
$\mu (\mathrm{mm}^{-1})$	0.414	2.726	0.413
θ Range (°)	2.06-28.40	3.70-60.09	1.56-25.85
Maximum indices: h	-14 to 8	-28 to 28	-15 to 12
k	-43 to 38	-9 to 5	-22 to 14
1	-14 to 14	-24 to 24	-21 to 22
Reflections measured	23182	6721	18725
Unique reflections {observed $F^2 > 2\sigma(F^2)$ }	8566 {7205}	6721 {5814}	7387 {6108}
R _{int}	0.0297		0.0494
$R \ [F^2 \ge 2\sigma(F^2)]^{\mathrm{a}}$	0.0383	0.0615	0.0530
wR_2 [all data] ^b	0.0766	0.1345	0.1086
Number of refined parameters	491	560	533
Largest difference map features (e $Å^{-3}$)	0.354, -0.590	1.631, -1.417	0.453, -0.693

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|.$ ^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2 / \sum [w(F_o^2)^2 \}^{1/2}.$

are given in Table 4 and crystal data appear in Table 3. Each molecule of 2 crystallises with a molecule of MeCN. The molecular structure is best described as a distorted trigonal pyramid with the pyridine of the diolate and the two imido groups in equatorial positions, i.e. 'eee' ligated L.

The ¹H NMR spectrum of **1** reveals an *AB* quartet at 3.86 ppm for the ligand backbone methylene units consistent with the diastereotopic proton environments in the 'aea' coordinated ligand. Contrastingly the room temperature ¹H NMR spectrum of **2** reveals a broadened singlet consistent with the 'eee' coordination geometry.

Meridional arrangements for L have been observed previously in the 6-coordinate complexes $[Mo(O)_2(L)-(Me_2SO)]$ and $[Os(O)_2(L)(H_2Nt-Bu)]$ [20,21]. In **2**, a non-crystallographic 2-fold-axis bisects the N(1)–Mo–N(2) angle between the imido groups and passes along the Mo–N(3) bond of the pyridinediolate. The bond parameters associated with the equatorial imido ligands are of particular interest to us here. The Mo–N distances are similar, viz Mo–N(1) = 1.710(5), Mo–N(2) = 1.727(4) Å, whereas the angles at the imido nitrogens are quite different, 168.8(4)° and 159.6(4)° (sum of angles = 328.4°), however, both imido ligands are still considered to be 'linear'.

Reaction of $[Mo(NAd)_2(Ot-Bu)_2]$ (prepared in situ from $[Mo(NAd)_2Cl_2(dme)]$ and LiOt-Bu) with LH₂ led to complex **2** together with trace amounts of yellow plate-like crystals, which were shown by X-ray diffraction to be the complex $[MoCl(NAd)_2(LH_{dehvd})]$ (**3**), where LH_{dehvd} is

the partially dehydrated ligand V. The structure of 3 is shown in Fig. 3, with selected bond lengths and angles given in Table 5. There is approximate trigonal bipyramidal geometry at the metal centre, with the pyridine of the chelate and two imido ligands equatorial. As in 1, the two imido ligands are quite different: Mo(1)-N(3) 1.724(3) Å/Mo(1)–N(3)–C(44) $170.9(3)^{\circ}$ versus Mo(1)– $N(2) 1.745(3) \text{ A/Mo}(1) - N(2) - C(34) 148.6(3)^{\circ}$; the latter is now in the range associated with bent imido groups (sum of angles = 319.5°). This bending could arise as a consequence of steric interactions with the pendant alkenyl arm of the chelate ligand. Pyridinediols have previously been found to act as HCl receptors, and the structure of the partially dehydrated ligand $V \cdot HCl$ (i.e., the HCl adduct of LH_{dehyd}) was shown to contain a Cl⁻ ion hydrogen-bonded to a protonated pyridine nitrogen atom. Interestingly, in order to achieve complete dehydration, neat H_3PO_4 had to be used at elevated temperatures [32].

3. Summary

We have described the synthesis and characterisation of two bis(imido)molybdenum complexes that differ in the coordination geometry of a tridentate [O,N,O] ligand: one of the complexes also has two electronically differing imido substituents. In this case the imido ligands with an electron-releasing tertiary-butyl substituent occupies the axial site within the trigonal bipyrimidal coordination





Fig. 2. (a,b) Two views of the molecular structure of **2** with H-atoms and MeCN of crystallisation omitted.

Table 4			
Selected bond lengths (Å) and angles (°) for 2			
Mo-N(1) 1.710(5)	Mo-N(2) 1.727(4)		
Mo-O(1) 1.995(3)	Mo-O(2) 2.020(4)		
Mo-N(3) 2.299(4)			
N(1)-Mo-N(2) 111.8(2)	N(1)-Mo-O(1) 101.22(18		
N(2)-Mo-O(1) 95.99(18)	N(1)-Mo-O(2) 94.99(19)		
N(2)-Mo-O(2) 100.05(18)	O(1)-Mo-O(2) 151.05(14)		
Mo-N(1)-C(1) 168.8(4)	Mo-N(2)-C(11) 159.6(4)		

geometry, the electron-withdrawing pentafluorophenyl imido group, the equatorial site. This would appear to be a favourable arrangement allowing the tertiary-butylimido group to maximise its π -donor group capacity through the formation of two π bonds. In the equatorial position, there is only a single $d\pi$ metal orbital available to overlap with the imido nitrogen π orbital thereby restricting the imido group to a single π -bond. A consequence of this is a formally sp²-hybridised nitrogen and an accordingly bent imido ligand. The structure of **2** lends further support to



Fig. 3. The molecular structure of 3 with H-atoms omitted.

Table 5				
Selected	bond lengths	(Å) and	angles (°) for $\boldsymbol{3}$	

Mo(1)–N(2) 1.745(3)
Mo(1)-Cl(1) 2.4196(11)
N(1)-Mo(1)-O(1) 76.25(10)
N(1)–Mo(1)–N(3) 147.41(13)
N(3)-Mo(1)-N(2) 107.93(14)
N(2)-Mo(1)-Cl(1) 108.03(10)
Mo(1)-N(3)-C(44) 170.9(3)

the observation that for electronically similar imido groups in identical coordination environments, especially when placed in direct competition for the available metal $d\pi$ orbitals, an imido bend angle in the range 150–180° is anticipated. The M–N–C angle then appears to be dictated by intramolecular steric effects and crystal packing forces, a consequence of a relatively shallow potential energy well for M–N–C bending when the two imido groups are in chemically equivalent sites and therefore in direct competition for the available metal π -orbitals.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham and of Imperial College. NMR spectra were recorded on a Varian VXR 400S spectrometer at 400.0 MHz (¹H), and 376.3 MHz (¹⁹F) at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent; IR spectra (nujol mulls, CsI windows), Perkin–Elmer 577 and 457 grating spectrophotometers. [Mo(Nt-Bu)(NC₆F₅)Cl₂(dme)], [Mo(NAd)-(NC₆F₅)Cl₂(dme)], [Mo(NAd)₂Cl₂(dme)] and LH₂ were prepared by the literature methods [27,21]. All other chemicals were obtained commercially and used as received unless stated otherwise.

4.2. Preparation of $[Mo(Nt-Bu)(NC_6F_5)L]$ (1)

To $[Mo(Nt-Bu)(NC_6F_5)(Ot-Bu)_2]$ [prepared in situ from $[Mo(Nt-Bu)(NC_6F_5)Cl_2(dme)]$ (1.50 g, 2.98 mmol) and LiOt-Bu (0.48 g, 6.00 mmol)] in ca. 50 cm³ diethyl ether was added LH₂ (1.37 g, 2.91 mmol). After stirring for 5-10 min, the volatiles were removed in vacuo. Toluene (ca. 40 cm^3) was added and the system was refluxed for 12 h. On cooling, volatiles were removed in vacuo and the residue was extracted with hot MeCN (40 cm^3). On standing at room temperature large yellow prisms of 1 Yield: 1.90 g, 80%. Anal. Calc. formed. for MoF₅O₂N₃C₄₃H₃₆ requires C, 63.2; H, 4.4; N, 5.1. Found: C, 63.4; H, 4.4; N, 5.0%. IR: 1600w, 1575w, 1494m, 1343m, 1312m, 1292m, 1261s, 1239m, 1211m, 1189m, 1093s, 1060s, 1023s, 977m, 960m, 947m, 916m, 892m, 875m, 801s, 770m, 753m, 733m, 724m, 701m, 658w, 638w, 619w, 607w, 600w, 592w, 565w, 512w, 497w, 484w, 452w, 427w, 417w, 404w. ¹H NMR (CDCl₃): δ 7.46–6.74 (several m, 23H, arylH), 3.86 (ABq, 4H, CH₂), 1.12 (s, 9H, C(CH₃)₃). ¹⁹F NMR (CDCl₃): δ -152.00 (m, 2F, *o*-F), -165.36 (tm,* 2F, ³J_{FF}) 18 Hz, ${}^{4}J_{FF}$ 3Hz, *m*-F), -167.44 (m, 1F, *p*-F). * triplet of multiplets.

4.3. Preparation of $[Mo(NAd)_2L]$ (2)

As for 1, using $[Mo(NAd)(NC_6F_5)Cl_2(dme)]$ (2.00 g, 3.42 mmol) and LiOt-Bu (0.54 g, 6.75 mmol) and LH₂ (1.60 g, 3.39 mmol) affording **2** · MeCN as golden-yellow prisms. Yield: 1.37 g, 89%. *Anal.* Calc. for MoO₂N₃-C₅₃H₅₅ · CH₃CN (sample dried for 12 h in vacuo) requires C, 73.2; H, 6.5; N, 6.2. Found: C, 73.7; H, 6.5; N, 6.1%. IR: 2359m, 2342m, 1737w, 1705w, 1654w, 1602w, 1580w, 1560w, 1500s, 1308w, 1242m, 1182w, 1119w, 1096w, 1062m, 1044s, 1027s, 984w, 963w, 924w, 890w, 812w, 784m, 752w, 701s, 606s. ¹H NMR (Acetone- d_6) δ : 7.65– 7.16 (several m, 23H, aryl*H*), 4.08 (bs, 4H, CH₂), 1.98 (m, 6H, CHad), 1.57 (m, 12H, CH₂ad), 1.56 (m, 12H, CH₂ad).

4.4. Preparation of $[MoCl(NAd)_2(L_{dehvd})]$ (3)

As for **1**, but using $[Mo(NAd)_2Cl_2(dme)]$ (0.93 g, 1.69 mmol) and LiOt-Bu (0.26 g, 3.25 mmol) with LH₂ (0.80 g, 1.70 mmol) affording on recrystallisation from hot acetonitrile **2** (0.61 g, 80%) and **3** (0.11 g, 15% based on Mo). For **3**, *Anal*. Calc. for MoClON₂C₄₃H₄₀ requires C, 70.5; H, 5.5; N, 3.8. Found: C, 69.4; H, 5.7; N, 3.8%. IR: 2359m, 2325m, 1654w, 1603m, 1568w, 1491m, 1302w,

1267w, 1233m, 1181w, 1122m, 1095m, 1053s, 1027m, 950m, 907w, 821w, 779m, 735w, 701s, 666s, 598s. ¹H NMR (CD₃CN) δ : 7.83–7.01 (several m, 23H, aryl*H*), 6.50 (d, 1H, C*H*), 4.09 (bs, 2H, C*H*₂), 1.97 (m, 18H, Ad*H*), 1.65 (m, 12H, Ad*H*).

4.5. X-ray crystallography

Crystallographic data and details of the data collection procedures and structure refinement for structures 1, 2 and 3 are presented in Table 3.

Data for 1 and 3 were collected on a Bruker AXS SMART 1K CCD area detector diffractometer using graphite monochromated Mo K α radiation (λ = 0.71073 Å) and narrow frames (0.3° in ω). Corrections were applied for Lorentz-polarisation effects and semiempirically for absorption based on symmetry equivalent and repeated data. Programs used were Bruker AXS SMART (machine control) and SAINT (frame integration) [33]. Data for 2 were collected on a Stoe-Siemens diffractometer with ω/θ scans and on-line profile fitting [34] with all machine-control calculations performed using Stoe DIF4 software and with graphite monochromated Cu Ka radiation ($\lambda = 1.54184$ Å). Corrections were applied for Lorentz-polarisation effects and semi-empirically for absorption using Ψ -scans. The structures were solved by direct methods for 1 and 3, (Patterson synthesis for 2) and refined by full-matrix least-squares on all data using F^2 values. All non-H atoms were refined anisotropically, H atoms, initially located in difference maps, were included using a riding model with U_{iso} equal to 1.2 times that of the carrier atom (1.5 times for methyl H). The program SHELXTL [35] was used for crystal structure solution and refinement and molecular graphics.

5. Supplementary material

CCDC 147054, 147055 and 147056 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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