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Synthesis of some very bulky N,N′-disubstituted amidines and initial studies of their coordination chemistry †

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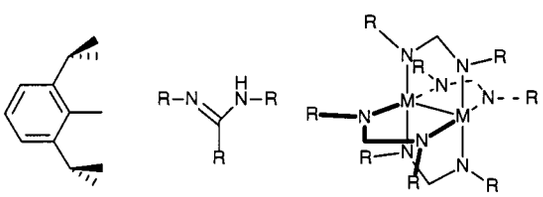
N,*N*′-Bis(2,6-diisopropylphenyl)-4-toluamidine, -4-anisylamidine and -acetamidine have been prepared for the first time from 2,6-diisopropylaniline and the acid chlorides *via* the corresponding imidoyl chlorides. The crystal structures of all three amidines were determined, indicating that the first is a disordered mixture of *Z-anti* and *E-syn* tautomeric forms, the second *Z-anti*, and the third *E-anti* in the solid state. Despite these differences, all three form identical coordination complexes with $Mo(CO)_3$ in which the ligand is in the *Z-anti* geometry, and the metal is π-coordinated to the *imino* 2,6-diisopropylphenyl ring, and the *amino* N–H unit is directed towards metal. The coordination mode was confirmed by single-crystal X-ray structure determination of the toluamidine and methylamidine complexes with $Mo(CO)_3$. In the case only of the methylamidine, an isolable intermediate is first formed in which the neutral amidine is coordinated in a monodentate fashion to an $Mo(CO)_5$ unit. The crystal structure of this complex shows that the ligand is in the *E-anti* geometry, with the *imino* nitrogen coordinated to Mo, *d*(Mo–N) = 2.352(2) Å. The structures are closely related in that the initial $Mo(CO)_5$ N-coordination sets up the metal for conversion to the more thermodynamically stable π-coordinated $Mo(CO)_3$ complex. The high steric bulk of these superamidine ligands is seen in the failure of any of them to form the metal–metal bonded $Mo_2(amidinate)_4$ complexes typically prepared using common, less bulky, amidines.

Introduction

So-called "super-bulky" substituents were originally developed in order to stabilize low-coordinate main-group elements of the 3rd period and beyond, allowing, to name one famous example, Yoshifuji to isolate the first compound containing a P=P double bond.[1] Such substituents have since found extensive application in many areas of main-group chemistry, including some of the 2nd period elements, *e.g.* boron.[2] Chemists who incorporate these substituents have always been aware that their large bulk may have created some perturbation of the bonds they were investigating, but in any case had no choice; lowering the bulk only slightly could lead to decomposition of the thermodynamically stable, but kinetically unstable bond, usually *via* a polymerization reaction. In view of these facts, it is surprising that more attention has not been given to making analogous compounds using these substituents with the elements *that do not intrinsically need them for kinetic stabilization*, *e.g.* the second-period elements such as C, N and O. Here direct comparison between analogous crowded and non-crowded molecules ought to be possible, and the influence of the steric bulk should be evident, and indeed often quantifiable.

It is our contention that the use of super-bulky substituents on these elements will also lead to unique patterns of reactivity, and in this work we report on the application of one such group, the 2,6-diisopropylphenyl (Dip) substituent[3] **1**, to N,N′-disubstituted amidine ligands **2**. Somewhat less bulky substituents (trimethylsilyl,[4] cyclohexyl[5]) have already found extensive application in amidinate metal complexes. We demonstrate that the super-bulky substituent does *not* prevent the synthesis of the ligands themselves, which have been prepared by fairly straightforward modifications of classical amidine synthetic procedures, nor do they fail to react with transition elements. Nevertheless, the course of the reactions with, in this case, $Mo(CO)_6$ differs significantly from that previously found for analogous non-bulky amidines, such as *N*,*N*′-diphenylbenzamidine, which was investigated many years ago by Cotton and Kilner.[6] In particular, whereas heating diphenylbenzamidine together with $Mo(CO)_6$ produced the quadruply-bonded dimolybdenum complex **3**, albeit in poor yield, we find that analogous reactions of the bulky superamidines produced two kinds of products, an N-coordinated $LMo(CO)_5$ complex and/or a half-sandwich $LMo(CO)_3$ complex in which one of the aryl rings of the ligand is π-complexed to $Mo(CO)_3$. The Cotton reaction is completely blocked, and there is no evidence of any metal complex in a higher oxidation state than Mo(0).



1 **2** **3**

Complexes of neutral monodentate amidines are rare.[7] Recently Bailey has reported Ag^+ and Co^{2+} complexes of triphenylguanidine (which can act as an amidine in monodentate or bidentate coordination modes),[8] and Cotton has reported several complexes of *N*,*N*′-diphenylformamidine with Ag^+ and divalent Mn, Co and Ni ions.[9] The only zero-valent Group 6 metal complex of a neutral amidine that we are aware of before this work is Raubenheimer's $(OC)_5W$–NH=C(NMe_2)Ph.[10] This complex is produced, *via* an imidate complex, by NH insertion into a metal–carbene bond, rather than through thermal reaction with the metal carbonyl, and in contrast to our $LMo(CO)_5$ complex, is found in solution in two isomeric forms.

† Part of this work was presented at the 31st International Conference on Coordination Chemistry, Vancouver, Canada, August 18–23, 1996.

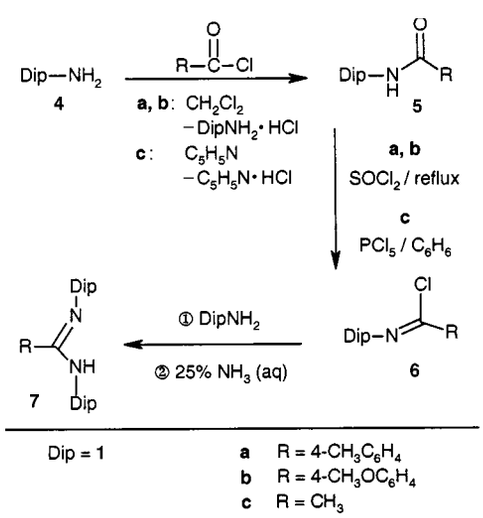
Table 1 Crystal data and structure refinement

Compound	**7a**	**7b**	**7c**	**8a**	**8c**	**9c**
Formula	$C_{32}H_{42}N_2$	$C_{32}H_{42}N_2O$	$C_{26}H_{38}N_2$	$C_{35}H_{42}MoN_2O_3$	$C_{29}H_{38}MoN_2O_3$	$C_{31}H_{38}MoN_2O_5$
M	454.68	470.68	378.58	634.65	558.55	614.57
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Scan mode	ω scans	φ oscillation	φ oscillation	φ rotation	φ oscillation	φ rotation
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C222_1$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	18.409(2)	18.269(2)	14.9260(10)	9.7485(12)	10.8448(11)	10.9975(10)
b/Å	9.9850(10)	10.1220(10)	20.1330(10)	10.5118(13)	19.285(2)	21.7750(18)
c/Å	17.6590(10)	17.899(2)	16.671(2)	18.577(3)	14.3146(14)	14.5403(13)
α/°				73.567(11)		
β/°	117.130(10)	117.717(9)		80.949(11)	101.993(8)	111.524(7)
γ/°				64.730(10)		
V/Å^3	2888.8(5)	2930.1(5)	5009.7(7)	1649.7(4)	2928.5(5)	3239.2(5)
Z	4	4	8	2	4	4
D_c/Mg m^{-3}	1.045	1.067	1.004	1.278	1.267	1.260
μ/mm^{-1}	0.060	0.064	0.058	0.432	0.477	0.442
F(000)	992	1024	1664	664	1168	1280
Crystal	Colourless block	Colourless block	Colourless block	Yellow plate	Yellow plate	Yellow prism
Reflections collected	6226	20572	22132	17169	61104	25416
Independent reflections	5026	5646	5435	6303	8322	6135
R_{int}	0.0275	0.0393	0.0466	0.0686	0.0655	0.0526
Final R indices [$I > 2\sigma(I)$] $R1$, $wR2$	0.0580, 0.1262	0.0561, 0.1570	0.0466, 0.1186	0.0418, 0.1029	0.0420, 0.1093	0.0370, 0.1001
R indices (all data) $R1$, $wR2$	0.1395, 0.1524	0.0769, 0.1728	0.0802, 0.1385	0.0627, 0.1120	0.0683, 0.1240	0.0512, 0.1086

Results and discussion

Ligand synthesis

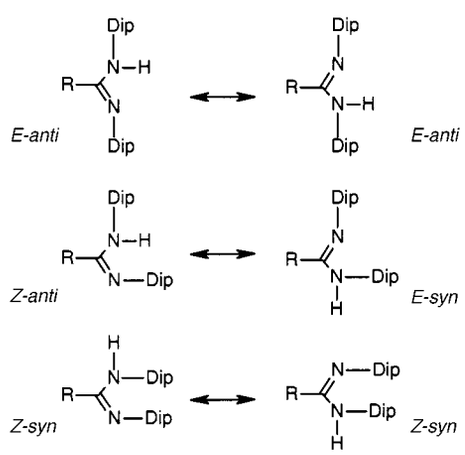
Our synthesis follows a classical route for the synthesis of *N*,*N*′-disubstituted amidines,[11] but each step of the procedure required extensive changes and optimization. The procedure is outlined in Scheme 1, and the particulars of each step are



Scheme 1

detailed in the Experimental section. The major modifications that were required reflected the high solubility of all diisopropylphenyl-containing compounds in non-polar solvents and/or their extreme insolubility in water. Commercially available 2,6-diisopropylaniline **4**, was converted to the corresponding amides of acetic **5c**, 4-methylbenzoic **5a**, or 4-methoxybenzoic acid **5b**, *via* the corresponding acid chlorides. Dehydration and chlorination produced the imidoyl-chlorides **6**, which for the aryl acids could be isolated, but for the acetic acid derivative was prepared *in situ*. The imidoyl-chlorides reacted directly with a second equivalent of **4** to produce the acid chloride salts of the desired amidine, which were readily converted to the free amidines **7**, using 25% aqueous ammonia. All of these compounds are new, and have been fully characterized by elemental analysis, mass spectrometry as well as ^{1}H and ^{13}C NMR spectroscopy. The details are given in the Experimental section. Using these procedures, superamidines can readily be prepared at low cost and in high yield on a reasonable scale for their further use as ligands in coordination chemistry.

Isomers and tautomers. Both isomers and tautomers are expected for N,N′-disubstituted amidines,[12] and it was immediately obvious from the ^{1}H NMR spectra of all three amidines that more than one isomer was present in solution. (In each case, the minor isomer is also undergoing a dynamic process in solution at room temperature; for simplicity, the NMR parameters of the major solution species only are reported in the Experimental section.) The possible isomers and their tautomeric forms are outlined in Scheme 2. The tautomers for the



Scheme 2

E-anti and *Z-syn* isomers are degenerate, while the *Z-anti* and *E-syn* isomers are related by tautomerism. It was not obvious from the spectroscopic information which isomers or tautomers we were dealing with. We therefore elected to measure the crystal structures of all three. The details of the crystallographic structure determinations are compiled in Tables 1 and 2. Ball-and-stick perspective diagrams of the amidines and the metal

Table 2 Selected interatomic distances (Å) and angles (°)

7a

N(1)–C(1)	1.344(3)	C(1)–N(1)–C(9)	129.9(2)
N(2)–C(1)	1.317(3)	C(1)–N(2)–C(21)	119.40(18)
Δ_{CN}[a]	0.027(6)	N(2)–C(1)–N(1)	120.4(2)
N(1)–C(9)	1.422(3)	N(2)–C(1)–C(2)	116.43(19)
N(2)–C(21)	1.429(3)	N(1)–C(1)–C(2)	123.1(2)
C(1)–C(2)	1.483(3)		

7b

N(1)–C(1)	1.3633(17)	C(1)–N(1)–C(9)	131.14(12)
N(2)–C(1)	1.3066(17)	C(1)–N(2)–C(21)	119.49(11)
Δ_{CN}[a]	0.057(3)	N(2)–C(1)–N(1)	121.38(12)
N(1)–C(9)	1.4294(17)	N(2)–C(1)–C(2)	117.04(11)
N(2)–C(21)	1.4262(17)	N(1)–C(1)–C(2)	121.53(11)
C(1)–C(2)	1.4890(18)		
N(1)–H(1)	0.92(2)		

7c

N(1)–C(1)	1.324(2)	C(1)–N(1)–C(9)	121.9(1)
N(2)–C(1)	1.330(2)	C(1)–N(2)–C(21)	122.9(1)
Δ_{CN}[a]	0.006(4)	N(2)–C(1)–N(1)	117.4(1)
N(1)–C(9)	1.427(2)	N(2)–C(1)–C(2)	121.2(2)
N(2)–C(21)	1.425(2)	N(1)–C(1)–C(2)	121.4(2)
C(1)–C(2)	1.493(3)	N(2)–H(1)–N(1′)	171(5)
N(2)–H(3)	0.97(2)		
N(1′)–H(3)	2.00(2)		

8a

C(1)–N(2)	1.297(4)	N(2)–C(1)–N(1)	123.3(2)
C(1)–N(1)	1.355(4)	N(2)–C(1)–C(2)	116.4(2)
Δ_{CN}[a]	0.058(8)	N(1)–C(1)–C(2)	120.3(2)
C(1)–C(2)	1.490(4)	C(1)–N(1)–C(9)	130.4(2)
C(9)–N(1)	1.440(4)	C(1)–N(2)–C(21)	126.7(2)
C(21)–N(2)	1.394(4)	C(43)–Mo(1)–C(41)	84.43(16)
N(1)–H(1)	0.89(1)	C(43)–Mo(1)–C(42)	83.09(15)
Mo(1)–C(43)	1.953(4)	C(41)–Mo(1)–C(42)	87.37(16)
Mo(1)–C(41)	1.948(4)	Mo(1)–H(1)–N(1)	152(2)
Mo(1)–C(42)	1.952(4)		
Mo(1)–H(1)	2.91(2)		

8c

N(1)–C(1)	1.358(3)	C(1)–N(1)–C(9)	125.6(2)
N(2)–C(1)	1.288(3)	C(1)–N(2)–C(21)	126.8(2)
Δ_{CN}[a]	0.070(6)	N(2)–C(1)–N(1)	124.6(2)
N(1)–C(9)	1.453(3)	N(2)–C(1)–C(2)	117.4(2)
N(2)–C(21)	1.395(3)	N(1)–C(1)–C(2)	118.0(2)
C(1)–C(2)	1.511(4)	C(35)–Mo(1)–C(34)	83.72(12)
N(1)–H(1)	0.88(3)	C(35)–Mo(1)–C(33)	86.34(14)
Mo(1)–C(35)	1.952(3)	C(34)–Mo(1)–C(33)	87.0(2)
Mo(1)–C(34)	1.955(3)	Mo(1)–H(1)–N(1)	155.34(8)
Mo(1)–C(33)	1.959(4)		
Mo(1)–H(1)	2.98(3)		

9c

N(1)–C(1)	1.302(3)	C(1)–N(1)–C(9)	115.80(19)
N(2)–C(1)	1.351(3)	C(1)–N(1)–Mo(1)	128.28(15)
Δ_{CN}[a]	0.049(6)	C(9)–N(1)–Mo(1)	115.83(14)
N(1)–C(9)	1.455(3)	C(1)–N(2)–C(21)	125.2(2)
N(2)–C(21)	1.439(3)	N(1)–C(1)–N(2)	120.0(2)
C(1)–C(2)	1.500(3)	N(1)–C(1)–C(2)	124.4(2)
N(2)–H(3)	0.890(7)	N(2)–C(1)–C(2)	115.6(2)
Mo(1)–N(1)	2.3519(19)	C(41)–Mo(1)–N(1)	173.10(13)
Mo(1)–C(41)	1.962(3)	C(45)–Mo(1)–N(1)	102.99(10)
Mo(1)–C(45)	2.016(4)	C(44)–Mo(1)–N(1)	96.77(10)
Mo(1)–C(44)	2.049(4)	C(42)–Mo(1)–N(1)	92.82(10)
Mo(1)–C(42)	2.062(4)	C(43)–Mo(1)–N(1)	86.93(10)
Mo(1)–C(43)	2.095(4)	Mo(1)–H(3)–N(2)	128(2)
Mo(1)–H(3)	2.88(2)		

[a] $\Delta_{CN} = d(C–N) - d(C=N)$.

complexes they form are presented in Fig. 1 and 2. Comparison with Scheme 2 indicates that no less than three of the four structural possibilities are present in the solid-state structures! Thus **7b** (Fig. 1b) is found in the solid state to be entirely *Z-anti* while **7a** (Fig. 1a) is disordered between the two tautomers

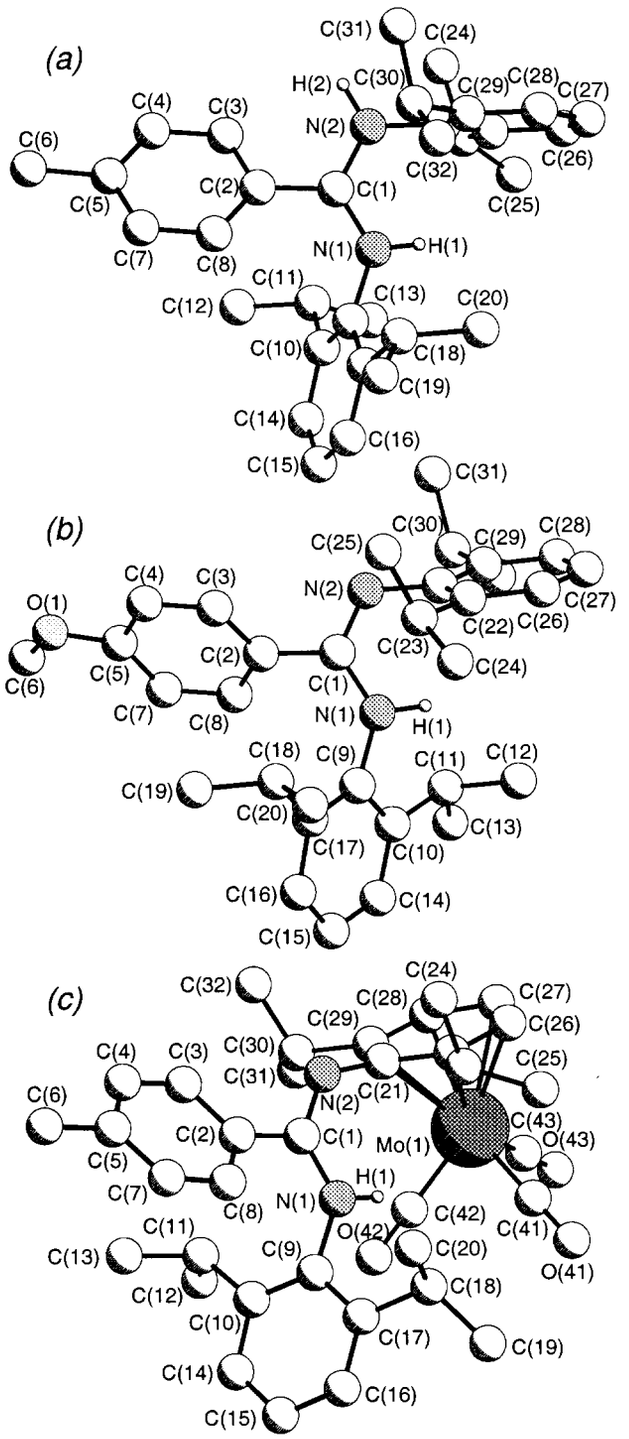


Fig. 1 PLUTO diagrams, showing the atom numbering schemes, of (a) **7a** {tautomers: H(1) occupancy 72%; H(2), 28%}, (b) **7b** {single tautomer}, and (c) **8a**.

Z-anti (72% refined occupancy) and *E-syn* (28% refined occupancy). On the other hand, **7c** (Fig. 2a) is found to be *E-anti* in the solid state in a strongly H-bonded dimeric structure, and consistently **7c** is much less soluble in non-polar solvents than **7a**,**b**.

Häfelinger and Kuske have compiled an up-to-date review of structural data on amidines. They define the parameter $\Delta_{CN} = d(C–N) - d(C=N)$ for the central N–C–N linkage found in all amidines.[12] This parameter ranges from 0 [*e.g.* in an *E-anti* hydrogen-bonded dimer of di(*para*-bromophenyl)formamidine] to 0.178 Å in an amidine where conjugation is minimized due to bulky substituents on nitrogen and carbon [$d(C–N) = 1.441(5)$; $d(C=N) = 1.263(5)$ Å]. This parameter is included in Table 2 for

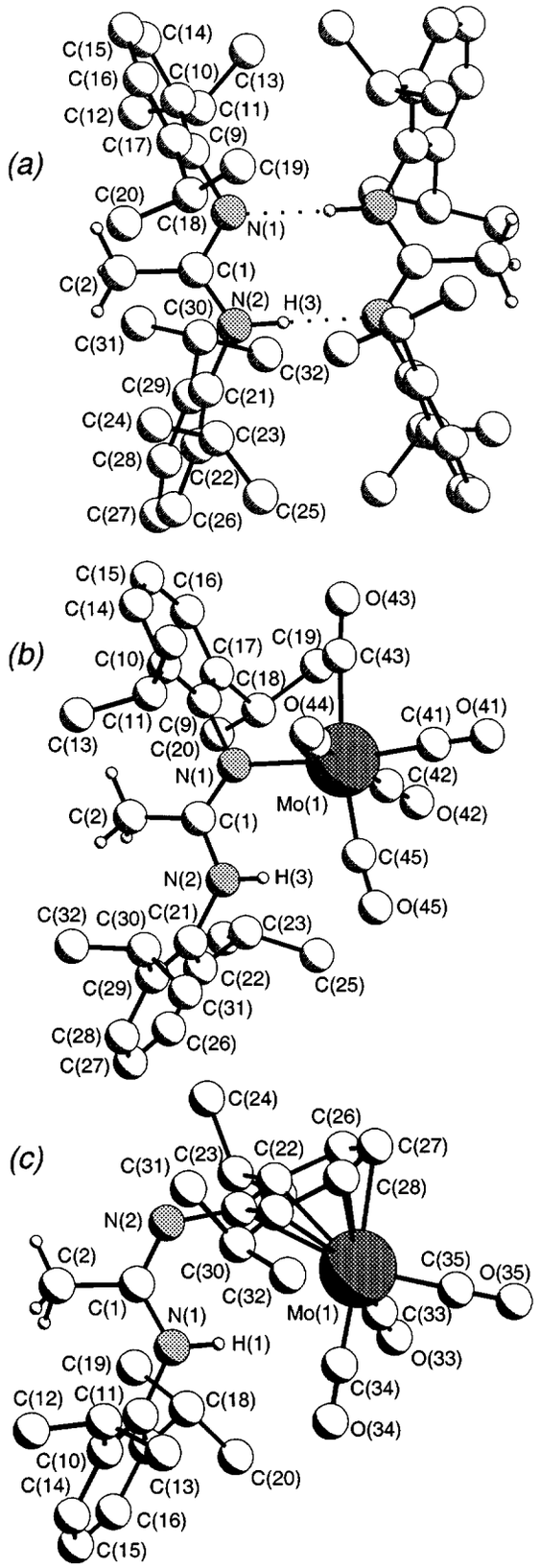
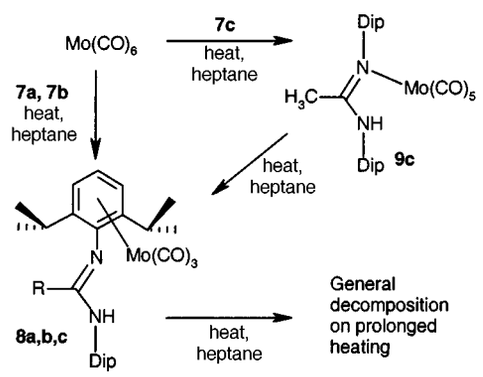


Fig. 2 PLUTO diagrams, showing the atom numbering schemes, of (a) **7c**, (b) **9c** and (c) **8c**. The hydrogen-bonded dimer of **7c** is shown by including a second molecule, located at $-x, y, \frac{1}{2} - z$, related to the first by a two-fold axis approximately perpendicular to the page.

the structures we have determined. As expected, Δ_{CN} is very small for the hydrogen-bonded dimer structure observed for **7c**, [in fact, at 0.006(4) Å the difference is statistically insignificant].[13] The pair of amidine molecules are related to each other by a two-fold axis approximately perpendicular to the N–C–N planes, but there is a considerable twist between the planes in the two molecules. Whether this serves to maximize H-bonding between the pyramidalized *amino* and planar *imino* nitrogen atoms, or whether it is a response to the high steric bulk of the diisopropylphenyl groups is unclear.

Δ_{CN} is much larger for **7b** which does not interact in the crystal with neighbouring molecules and shows no evidence of H-bonding. The value 0.057 Å is identical to the average of two values from independent molecules of *N*,*N*′-diphenylbenzamidine, which also crystallizes in the *Z-anti* structure.[12] However, **7a**, which is almost isostructural to **7b**, has the very low Δ_{CN} value of 0.027 Å. This observation caused us to look carefully at the electron-density map around the nitrogen atoms, and we were able to refine a disorder model in which about ¼ of the molecules have the hydrogen on N(2), and ¾ on N(1). This means that *both* tautomers, *Z-anti* and *E-syn*, co-exist in a single crystal of **7a**. In order to verify this unprecedented result, we have determined this structure from two data sets collected on different crystals, and find virtually the same ratios of the two tautomers from both structure determinations. As mentioned above, NMR spectra show conclusively that **7** exists in solution in two isomeric forms, irrespective of which isomer they crystallize in. The relative proportions of the isomers seem to be independent of sample origin, so that an equilibrium seems to exist. At this time, we are unable to make a definitive correlation between the solid state and solution structures. However, we note that two of the ligand geometries (*Z-anti* and *E-anti*) are found in the metal complexes discussed below, but that *each metal complex* is isomerically pure in solution by NMR! Thus metal coordination influences the geometry of the ligands in a very definite way.

Reaction with $Mo(CO)_6$. Amidines **7a**–**c** were heated with $Mo(CO)_6$ in refluxing *n*-heptane under an atmosphere of N_2 (Scheme 3). The course of the reaction was easily monitored by



Scheme 3

solution infrared spectroscopy and we observed that **7a**,**b** reacted slowly, with little evidence of any intermediate, to give the final products, bright yellow crystalline solids which were produced in 54 (**8a**) and 65% (**8b**) yield. The structure of both compounds was indicated by ^{1}H NMR and IR spectroscopy to be a half-sandwich "piano-stool" complex of $Mo(CO)_3$, rather than a nitrogen coordination complex. In the ^{1}H NMR spectrum, the signals due to the aromatic hydrogen atoms of one of the diisopropylaniline groups is shifted over 2 ppm upfield, while the other signals changed little. The solution IR (Table 3) consisted of three bands in the carbonyl stretching region, a very strong singlet at about 1966 cm^{-1}, and a slightly less intense doublet at about 1885 cm^{-1}. This is the pattern expected for a *fac*-octahedral tricarbonyl metal complex with highly asymmetric co-ligands.[13]

On the other hand, when **7c** reacted with $Mo(CO)_6$ under identical conditions, solution IR spectroscopy showed the initial formation of a different set of signals, which grew in rapidly at the reflux temperature, and reached a maximum after *ca.* 1 h.

Table 3 Solution IR data[a]

Compound	ν(N–H)/cm^{-1}	ν(N–C–N)/ cm^{-1}	ν(C≡O)/cm^{-1}
7a	3431, 3366	1620	—
7b	3431, 3366	1620	—
7c	3391, 3378, 3366, 3350	1643	—
8a	3216[b]	1615	1966, 1896, 1879
8b	3216[b]	1614	1965, 1896, 1879
8c	3193[b]	1640	1966, 1896, 1876
9c	3312[b]	1603, 1582	2072, 1989, 1942, 1931, 1908

[a] *n*-Heptane solution in 0.2 mm NaCl solution cell, unless otherwise noted. [b] $CHCl_3$ solution in 0.2 mm NaCl solution cell; these weak bands are not observed in *n*-heptane because of limited solubility of the complexes.

If heating was continued these signals gradually disappeared to be replaced by a final set of peaks similar to those of the piano stool complexes **8a**,**b**. The intermediate thus is consumed more rapidly than $Mo(CO)_6$ itself. All the peaks were identified by comparison with spectra of the purified products and those of the starting materials. When the reaction was quenched after 1.5 h at reflux, we were able to crystallize mixtures of $Mo(CO)_6$, **8c** and the intermediate product. The $Mo(CO)_6$ could be sublimed out of the mixture, and recrystallization from *n*-heptane by cooling saturated solutions to −30 °C *without* heating, affording pale yellow crystals of the intermediate, **9c**, in 47% yield. The carbonyl stretching frequencies in the IR spectrum are consistent with a $LMo(CO)_5$ complex, in which L is an asymmetrical ligand,[14] and the ^{1}H NMR shows the *absence* of the upfield shift in the aromatic region indicative of π-coordination. Further indication that this species is nitrogen-coordinated was provided by the solution IR data in the C=N region. In the free ligand, an asymmetrical doublet is observed at 1643 cm^{-1}. This peak is found, essentially unchanged, at 1640 cm^{-1} in **8c** (Table 3). However, in **9c** we find instead two well-separated bands at 1603 and 1582 cm^{-1}, indicating that in the complex the energies of the N–C–N bonds have been affected. Final confirmation of the bonding mode came from a single-crystal structure.

In a separate experiment, a heptane solution of **9c** was heated and monitored by solution IR spectroscopy. This resulted in direct conversion to **8c**, along with some decomposition, indicating that **9c** is a genuine intermediate on the way to **8c**. In another experiment, we heated **9c** in heptane under one atmosphere of carbon monoxide. Not only did the CO inhibit the formation of **8c**, it also displaced the ligand from **9c**, so that slowly $Mo(CO)_6$ and the free amidine formed in solution.

Crystal structures of the metal complexes

For **8**, IR and NMR evidence indicated the presence of an $Mo(CO)_3$ group on one of the diisopropylaniline rings. However, there was no clear indication of which of the two, the *amino* or the *imino* ring, was involved, no information on the geometry of the amidine, nor the choice of face of the ring occupied by the $Mo(CO)_3$ group. What was clear from the NMR was that each metal complex contained only one amidine configuration, but differences in spectral features between the ligands with aryl- and alkyl-substituents on the amidinyl C atom were too large to allow us to make any definitive assignments of ligand conformation in a given complex, except that **8a** and **8b** have the same configuration. For **9c**, we also needed proof of the coordination mode. We have therefore determined the single-crystal structures of **8a**,**8c** and **9c**.

The structure of **8a** is presented in Fig. 1c. The structure resembles a "baseball catcher's mitt", in which the amidine ligand, itself in the *Z-anti* tautomer, has caught the $Mo(CO)_3$ fragment with the inside face of the *imino*-bearing ring. With respect to the C(1)=N(2) bond, the metal complex also has *Z* symmetry. The N–H of the *amino* group corresponds to the "catcher's thumb", and there is a close contact of 2.91(2) Å between H(1) and Mo, less than a reasonable guess at the sum of their van der Waals' radii. Further evidence for a perturbation of the metal coordination environment by the N(1)–H(1) unit is that the V-shaped side of the $(CO)_3$ piano-stool is twisted towards, and bisected by, this unit. The C(41)–Mo–C(42) angle is significantly larger than the other angles involving the carbonyl ligands. Indeed, the metal could just as well have coordinated to the opposite face of the same ring, with significantly less steric hindrance, but prefers the inner coordination pocket. The balance of the evidence suggests a secondary coordination effect by the *amino* unit, the "thumb" of the "catcher". The structure of **9c** is shown in Fig. 2b. The $Mo(CO)_5$ group is coordinated by a single nitrogen atom, the *imino*-N, which is the more basic atom in the amidine ligand.[7] The ligand is in the *E-anti* configuration (*i.e.* the same isomer as found in the hydrogen-bonded dimer structure of **7c**) but the metal complex has *Z* symmetry with respect to the C(1)=N(1) bond. That the hydrogen bonds are now broken is evident in the large change in the two C–N bond distances, which are now clearly differentiated for the single and the double bond (Δ_{CN} = 0.049 Å). The ^{1}H NMR shows that only one isomer is present in solution, which we presume to be the same as in the crystal. This is in contrast to $(OC)_5W$–NH=C(NMe_2)Ph, for which *non-inter-converting* "*E*" and "*Z*" isomers are formed in solution in a 3:1 ratio.[10] A structure has been obtained for the *E* isomer, and interestingly Δ_{CN} = 0.05(1) Å, statistically identical to that in **9c**.[7] The ν(C=N) values of **9c** and this tungsten complex are also very similar. However, the Mo–N bond length in **9c** is significantly longer at 2.352(2) *vs.* 2.243(5) Å for the W–N bond; a difference accentuated by the (slightly) greater radius of W over Mo. It is certainly possible that the great steric bulk of the superamidine is significantly weakening the Mo–N bond, but we hesitate to draw premature conclusions. Preliminary evidence suggests that the $W(CO)_5$ complex of **7c** has significantly greater thermal stability than **9c**, so that a difference exists between these two metals that cannot be ignored.

The biggest surprise in our structure determinations, unanticipated from the NMR data, was that of **8c**, which strongly resembles that of **8a**, the "Catcher's mitt" type, in which the ligand has isomerized to the *Z-anti* geometry (Fig. 2c). In retrospect, the distinct differences in the NMR spectra of **8c** compared to **8a**,**b** are probably due to ring-current shielding effects perpendicular to the $CH_3C_6H_4$ and $CH_3OC_6H_4$- rings on the amidinyl C atom. The structures of **8c** and **9c** provide an appealing visual mechanism for the reaction, in which an $Mo(CO)_5$ unit held by the *imino* nitrogen close to an electron-rich benzene ring (activated by two C_3H_7 substituents) loses two further CO ligands and slides over to the tripodal ligand environment of the aryl ring. All the spectroscopic evidence suggests that only one isomeric form exists in solution for each of these metal complexes, and since we have confirmed that purified **9c** converts smoothly to **8c**, the change from η^1-N to η^6-C coordination evidently induces *E-anti* to *Z-anti* ligand isomerization. The structural studies also suggest one possible reason why the methylamidine **7c** alone forms the N-coordinated complex **9c**, since this is the one ligand which crystallizes preferentially in the *E-anti* form. This hydrogen-bonded dimer is appreciably less soluble than the other amidine ligands, and it is possible that complexation of the *E-anti* geometry occurs before isomerization of the ligand in heptane solution, and that this leads to the formation of the metastable **9c** in the case of ligand **7c** alone.

Comparison to previous results

In 1975, Cotton, Kilner *et al.* reported the results of reacting $Mo(CO)_6$ in refluxing light petroleum (bp 100–120 °C) with

N,*N*′-diphenylbenzamidine.[6] The only product which could be isolated was a red compound, which *precipitated* from the hot solution in 16% yield. X-Ray crystallography confirmed this material to be a quadruply-bonded $Mo_2(amidine)_4$ species. In the same paper they reported, however, that under similar reaction conditions $Cr(CO)_6$ produced an *insoluble* red compound which did not appear to retain any carbonyl groups as well as a soluble yellow product with two intense IR signals at 1964 and 1883 (br) cm^{-1} and a mass spectrum which fitted for $LCr(CO)_3$.[6] The structure of this compound was not further investigated, but it may well be similar to that of **8**. We could not detect any evidence of a $Mo_2(amidine)_4$ species using ligands **7**, and we attribute this to the much greater steric requirements of the superamidines. Prolonged heating of solutions of **8** lead to the slow formation of a black tar from which no recognizable compounds could be isolated. Increasing the ratio of amidine to $Mo(CO)_6$ up to the 2:1 ratio required for $Mo_2(amidine)_4$ has no effect on product distribution, but complicates the work-up due to the presence of unreacted amidine.

Conclusions

In this work we have demonstrated that superamidines bearing very bulky substituents are accessible using highly-modified standard organic synthetic routes. The amidines exist in a variety of isomeric forms, which seem to be interchangeable. Secondly, in thermal reactions with $Mo(CO)_6$, these superamidines behave very differently from *N*,*N*′-diphenylbenzamidine, the closest non-bulky model ligand. Thus we observe for the superamidines two coordination modes, (1) monodentate *imine*-N coordination and (2) π-aryl coordination, which are not observed for diphenylbenzamidine. The metal–ligand interaction is very specific, such that consistently only one ligand geometry is found in each type of metal complex. Conversely, the superamidines did not undergo the redox reaction with the metal that the *N*,*N*′-diphenyl ligand undergoes to form M–M quadruply-bonded species. The competition experiments with CO indicate that **7c** is a weak monodentate ligand.

We are continuing our studies on thermal reactions with the other Group 6 hexacarbonyls. Initial indications are that similar products form, although the reactions proceed markedly slower and the products are more difficult to purify. We expect to see other consequences of steric bulk in our continued exploration of the coordination chemistry of superamidines, including superamidinate anions.

Experimental

General

2,6-Diisopropylaniline (Accros, Aldrich), *para*-toluoyl chloride (Accros, Aldrich), *para*-anisoyl chloride (Aldrich), acetyl chloride (Aldrich) and molybdenum carbonyl (Strem) were commercial products, and used as received, except that the aniline was vacuum distilled and stored under nitrogen before use. Solvents were reagent grade, and distilled from sodium wire (toluene), P_2O_5 (CH_2Cl_2) or $LiAlH_4$ (*n*-heptane). Pyridine was dried over molecular sieves. Reactions involving metal carbonyl derivatives were performed under an atmosphere of purified N_2 using a dry-box, Schlenk ware and vacuum-line techniques; all other procedures were performed in vessels open to the atmosphere but protected by $CaCl_2$ drying tubes. Infrared spectra were recorded on a BOMEM MB102 Fourier transform spectrometer, and are KBr pellets unless otherwise specified. NMR spectra were acquired at 250.13 (^1H) and 62.90 (^{13}C) MHz on a Bruker AC250-F spectrometer, and are in $CDCl_3$ unless otherwise specified. Mass spectra were recorded by the Mass Spectrometry Center, University of Alberta, Canada and in the Fachbereich Chemie, Universität Kaiserslautern. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ, USA and by the analytical services of the Fachbereich Chemie, Universität Kaiserslautern.

Preparation of 4-$CH_3C_6H_4C(O)NH(2,6\text{-}^iPr_2C_6H_3)$ 5a

To 2,6-diisopropylaniline (20.0 g, 113 mmol) in 70 mL of dry CH_2Cl_2 was added 8.7 g (56.3 mmol) *para*-toluoyl chloride in 45 mL CH_2Cl_2 with stirring. A precipitate formed. The mixture was heated at reflux for 20 h. After cooling a white solid was filtered off and washed with ice-cold CH_2Cl_2 and dried *in vacuo* to give 12.5 g (42.3 mmol, 75% yield) of **5a** which was pure by NMR. An analytical sample was obtained by recrystallization from toluene, mp 218 °C (decomp.) (Calc. for $C_{20}H_{25}NO$: C, 81.3; H, 8.53; N, 4.7. Found: C, 81.1; H, 8.4; N, 4.7%). IR: ν(N–H) 3341, ν(C=O) 1644 cm^{-1}. ^1H NMR: δ 7.85–7.82 (m, 2 H), 7.4 (s, 1 H, concentration dependent), 7.37–7.20 (m, 5 H), 3.14 (hept, 6.8, 2 H), 2.45 (s, 3 H), 1.22 (d, 6.8 Hz, 12 H). ^{13}C NMR: δ 167.02, 146.63, 142.29, 131.796, 131.63, 129.53, 128.51, 127.42, 123.64, 29.04, 23.79, 21.66. MS: *m*/*z* 295 (M^+, 100); 252 ($M - {}^iPr^+$, 32); 176 ($C_6H_3{}^iPr_2NH^+$, 38); 119 ($CH_3C_6H_4CO^+$, 14%).

Preparation of 4-$CH_3OC_6H_4C(O)NH(2,6\text{-}^iPr_2C_6H_3)$ 5b

Prepared in the same way as **5a** in 78% yield, mp 273–274 °C (decomp.) (Calc. for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.23; H, 8.09; N, 4.46%). IR: ν(N–H) 3328, ν(C=O) 1640 cm^{-1}. ^1H NMR: δ 7.85 (d, 8.9, 2 H) 7.43 (s, 1 H, concentration dependent), 7.36–7.18 (m, 3 H), 6.93 (d, 8.9, 2 H), 3.87 (s, 3 H), 3.12 (hept, 6.9, 2 H), 1.19 (d, 6.9, 12 H). ^{13}C NMR: δ 166.41, 162.42, 146.5, 131.51, 129.08, 128.33, 126.77, 123.50, 113.95, 55.49, 28.89, 23.65. MS: *m*/*z* 311.18839 (M^+, 58); 268 ($M - {}^iPr^+$, 35); 176 ($C_6H_3{}^iPr_2NH^+$, 70); 134 ($CH_3OC_6H_4CO^+$, 100%).

Preparation of $CH_3C(O)NH(2,6\text{-}^iPrC_6H_3)$ 5c

Neat acetyl chloride (8.03 mL, 113 mmol) was carefully pipetted into a solution of 2,6-diisopropylaniline (20.0 g, 113 mmol) in 200 mL of dry pyridine (**CAUTION**: vigorous reaction, use cooling), whereupon the mixture was refluxed for 3 h. The solvent was removed, and the residues taken up in 200 mL CH_2Cl_2 and washed twice with 200 mL water. After drying and removal of solvent, the crude product was recrystallized from 100 mL toluene to give 16.7 g of colourless crystals (76.1 mmol, 68% yield), mp 192–196 °C (Calc. for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.58; H, 9.45; N, 6.45%). IR: ν(N–H) 3249, ν(C=O) 1647 cm^{-1}. ^1H NMR: δ 7.36–7.14 (m, 3 H), 7.05 (s, 1 H, concentration dependent), 3.18 (32%, hept, 6.9, 2 H), 3.07 (68%, hept, 6.9, 2 H), 2.15 (68%, s, 3 H), 1.72 (32%, s, 3 H), 1.24 (32%, d, 6.9, 6 H), 1.18 (68%, d, 6.9, 12 H), 1.16 (32%, d, 6.9 Hz, 6 H). ^{13}C NMR: 32% isomer δ 173.87, 146.63, 132.17, 128.92, 123.78, 28.33, 22.9, 22.63, 19.99; 68% isomer δ 169.77, 146.19, 131.3, 128.16, 123.25, 28.61, 24.29, 23.51. MS: *m*/*z* 219.16244 (M^+, 91); 204 ($M - CH_3^+$, 63); 176 ($C_6H_3{}^iPr_2NH^+$, 100); 162 ($C_{11}H_{16}N^+$, 70); 134 ($C_9H_{12}N^+$, 28%).

Preparation of 4-$CH_3C_6H_4C(Cl)N(2,6\text{-}^iPr_2C_6H_3)$ 6a

Complex **2a** (12.4 g, 42.9 mmol) was refluxed in 9 mL of $SOCl_2$ (excess) for 1.5 h (oil bath at 80–90 °C), after which the bath temperature was raised to 140 °C and the remaining $SOCl_2$ was distilled off. The residues were vacuum distilled (air condenser, **CAUTION**: solid product may block narrow take-off adapters), bp 135–140 °C at 1×10^{-2} Torr. On cooling a bright yellow solid was obtained which was analytically pure **6a** (12.6 g, 40.1 mmol, 96% yield) , mp 61–63 °C (Calc. for $C_{20}H_{24}ClN$: C, 76.5; H, 7.7; N, 4.5. Found: C, 76.5; H, 7.7; N, 4.5%). ^1H NMR: δ 8.10 (d, 8.3, 2 H), 7.31 (d, 8.3, 2 H), 7.18 (s, 3 H), 2.81 (hept, 6.9, 2 H), 2.45 (s, 3 H), 1.21 (d, 6.9, 6 H), 1.15 (d, 6.9 Hz, 6 H). ^{13}C NMR: δ 143.92, 143.44, 142.77, 136.82, 132.38, 129.44,

124.77, 123.05, 28.67, 23.30, 22.88, 21.47. MS: *m*/*z* 313 (M^+ on ^{35}Cl, 14); 278 ($M - Cl^+$, 100%).

Preparation of 4-$CH_3OC_6H_4C(Cl)N(2,6\text{-}^iPr_2C_6H_3)$ 6b

Prepared by the same method as **6a**, yellow solid, bp 160–170 °C at 1×10^{-2} Torr (97% yield), mp 104–105 °C (Calc. for $C_{20}H_{24}ClNO$: C, 72.82; H, 7.33; N, 4.25. Found: C, 72.80; H, 7.46; N, 4.32%). ^{1}H NMR: δ 8.17 (d, 9.9, 2 H), 7.17 (s, 3 H), 6.97 (d, 9.9, 2 H), 3.85 (s, 3 H), 2.84 (hept, 6.9, 2 H), 1.22 (d, 6.9, 6 H), 1.16 (d, 6.9 Hz, 6 H). ^{13}C NMR: δ 163.00, 143.99, 143.15, 137.12, 131.42, 127.55, 124.89, 123.14, 113.96, 55.59, 28.79, 23.41, 23.01. MS: *m*/*z* 329.15447 (M^+ on ^{35}Cl, 14); 294 ($M - Cl^+$, 100); 121 ($C_8H_9O^+$, 15%).

Preparation of 4-$CH_3C_6H_4C(NC_6H_3{}^iPr_2\text{-}2,6)NH(2,6\text{-}^iPr_2C_6H_3)$ 7a

To 9.00 g (28.7 mmol) **6a** in 70 mL dry toluene was added 5.08 g (28.7 mmol) 2,6-diisopropylaniline, and the mixture was refluxed for 20 h. Removal of the solvent and drying the residues *in vacuo* gave a quantitative yield of **7a**·HCl. This material was dissolved in 100 mL 95% ethanol and treated with six 15 mL portions of 25% aqueous NH_3. The beige solid was filtered off and air dried for 20 h. Recrystallization from 65 mL 95% ethanol produced off-white crystals of **7a** (8.72 g, 19.2 mmol, 67% yield). An analytical sample was obtained after a second recrystallization, mp 139–140 °C (Calc. for $C_{32}H_{42}N_2$: C, 84.5; H, 9.3; N, 6.2. Found: C, 84.6; H, 9.2; N, 6.1%). IR: ν(N–H) 3428, 3366, ν(N–C–N) 1613 cm^{-1}. ^{1}H NMR: δ 7.29–6.97 (m, 10H), 5.67 (s, 1 H), 3.30–3.31 (m, 4 H), 2.27 (s, 3 H), 1.34 (d, 7.0, 6 H), 1.23 (d, 6.7, 6 H), 0.98 (d, 6.7, 6 H), 0.88 (d, 6.8 Hz, 6 H). ^{13}C NMR: δ 153.39, 145.14, 143.89, 139.29, 139.08, 134.12, 132.13, 128.68, 128.31, 127.36, 123.30, 123.17, 28.51, 28.32, 25.11, 24.37, 22.47, 22.37, 21.23. MS: *m*/*z* 454 (M^+, 67); 411 ($M - {}^iPr^+$, 28); 278 ($M - C_6H_3{}^iPr_2NH^+$, 100); 177 ($C_6H_3{}^iPr_2NH_2^+$, 86); 162 ($C_6H_3{}^iPr_2^+$, 14%).

Preparation of 4-$CH_3OC_6H_4C(NC_6H_3{}^iPr_2\text{-}2,6)NH(2,6\text{-}^iPr_2C_6H_3)$ 7b

Produced from **6b** as for **7a**, off-white crystals (64% yield), mp 164–165 °C (Calc. for $C_{32}H_{42}N_2O$: C, 81.66; H, 8.99; N, 5.95. Found: C, 81.80; H, 8.83; N, 6.00%). IR: ν(N–H) 3426, 3368, ν(N–C–N) 1615 cm^{-1}. ^{1}H NMR: δ 7.35–6.70 (m, 10H), 5.66 (s, 1 H), 3.74 (s, 3 H), 3.28–3.11 (m, 4 H), 1.34 (d, 6.9, 6 H), 1.23 (d, 6.7, 6 H), 0.99 (d, 6.8, 6 H), 0.90 (d, 6.8 Hz, 6 H). ^{13}C NMR: δ 160.23, 152.89, 145.11, 143.94, 139.30, 134.18, 130.27, 127.49, 127.35, 123.62, 123.25, 123.15, 112.99, 28.50, 28.33, 25.07, 24.37, 22.44. MS: *m*/*z* 470.3301 (M^+, 24); 427 ($M - {}^iPr^+$, 30); 294 ($M - C_6H_3{}^iPr_2NH^+$, 100); 177 ($C_6H_3{}^iPr_2NH_2^+$, 8); 121 ($C_8H_9O^+$, 19%).

Preparation of $CH_3C(NC_6H_3{}^iPr_2\text{-}2,6)NH(2,6\text{-}^iPr_2C_6H_3)$ 7c

11.45 g PCl_5 (55.0 mmol) was dissolved in 50 mL dry benzene with heating under N_2. To the cooled solution was added 10.9 g **5c** (50.0 mmol), and the mixture was refluxed for 30 min, until gas evolution ceased. To the cooled, N_2-flushed, solution was added 8.86 g 2,6-diisopropylaniline in 50 mL of dry benzene, whereupon the mixture was again refluxed, for 20 h. On cooling, an off-white precipitate of **7c**·HCl formed, which was filtered off and washed with hexanes. The free base was liberated as before, and recrystallization from 900 mL 95% ethanol produced white crystals of **7c** (14.3 g, 37.8 mmol, 75% yield). An analytical sample was obtained after a second recrystallization, mp 227–230 °C (Calc. for $C_{26}H_{38}N_2$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.60; H, 9.96; N, 7.53%). IR: ν(N–H) 3622–3116, ν(N–C–N) 1641 cm^{-1}. ^{1}H NMR: δ 7.29–7.04 (m, 6H), 5.40 (s, 1 H), 3.31–3.10 (m, 4 H), 1.88 (s, 3 H), 1.40–1.01 (m, 24 H). ^{13}C NMR: δ 153.81, 147.04, 143.05, 139.77, 133.38, 128.37, 125.30, 123.63, 123.19, 28.25, 28.05, 24.69, 24.60, 23.55, 23.40, 23.23, 22.52, 19.64. MS: *m*/*z* 378.30313 (M^+, 18); 335 ($M - {}^iPr^+$, 28); 202 ($M - C_6H_3{}^iPr_2NH^+$, 100); 177 ($C_6H_3{}^iPr_2NH_2^+$, 8%).

Preparation of η^6-[4-$CH_3C_6H_4C(NC_6H_3{}^iPr_2\text{-}2,6)NH(2,6\text{-}^iPr_2C_6H_3)]Mo(CO)_3$ 8a

500 mg (1.1 mmol) of **7a** and 290 mg (1.1 mmol) of $Mo(CO)_6$ were loaded under N_2 into a Schlenk tube. 27 mL of dry *n*-heptane was then added, and the mixture heated to reflux. Progress of the reaction was monitored by solution IR, and heating discontinued after 28 h. Collection of the green-tinged yellow crystals provided 380 mg of **8a** [0.60 mmol, 54% yield, mp 130 °C (decomp.)]. Recrystallization from 12 mL of *n*-heptane provided bright yellow analytically pure crystals (Calc. for $C_{35}H_{42}MoN_2O_3$: C, 66.24; H, 6.67; N, 4.41. Found: C, 66.46; H, 6.77; N, 4.26%). IR: ν(N–H) 3426, 3194, ν(C≡O) 1952, 1871, ν(N–C–N) 1613 cm^{-1}. ^{1}H NMR: δ 8.20 (s, 1 H), 7.29–6.96 (m, 7 H), 5.79–5.66 (m, 3 H), 3.17 (hept, 6.8, 2 H), 2.85 (hept, 6.9, 2 H), 2.27 (s, 3 H), 1.28 (d, 6.9, 6 H), 1.27 (d, 6.9, 6 H), 1.20 (d, 6.8, 6 H), 0.86 (d, 6.8 Hz, 6 H). ^{13}C NMR spectrum not obtained due to sample instability. MS: *m*/*z* 636.22411 (M^+ based on ^{98}Mo, 0.05); 454 (L^+, 51%); 411 ($L - {}^iPr^+$, 54); 278 ($L - C_6H_3{}^iPr_2NH^+$, 100); 177 ($C_6H_3{}^iPr_2NH_2^+$, 24); 162 ($C_6H_3{}^iPr_2^+$, 14).

Preparation of η^6-[4-$CH_3OC_6H_4C(NC_6H_3{}^iPr_2\text{-}2,6)NH(2,6\text{-}^iPr_2C_6H_3)]Mo(CO)_3$ 8b

Prepared from 500 mg of **7b** in a similar manner to **8a**. Yield 447 mg (0.69 mmol, 65%) of bright yellow crystals, mp 130–135 °C (decomp.) (Calc. for $C_{35}H_{42}MoN_2O_4$: C, 64.61; H, 6.51; N, 4.31. Found: C, 64.76; H, 6.64; N, 4.11%). IR: ν(N–H) 3436, 3219, ν(C≡O) 1950, 1871, ν(N–C–N) 1613 cm^{-1}. ^{1}H NMR: δ 8.18 (s, 1 H), 7.26 (d, 9, 2 H), 7.29–7.06 (m, 3 H), 6.69 (d, 9, 2 H), 5.79–5.66 (m, 3 H), 3.74 (s, 3 H), 3.17 (hept, 6.8, 2 H), 2.84 (hept, 6.9, 2 H), 1.28 (d, 6.9, 6 H), 1.27 (d, 6.7, 6 H), 1.20 (d, 6.8, 6 H), 0.88 (d, 6.8 Hz, 6 H). ^{13}C NMR spectrum not obtained due to sample instability. MS: *m*/*z* 652.22032 (M^+ based on ^{98}Mo, 1); 568 ($M^+ - 3CO$, 6); 470 (L^+, 13); 454 ($L - CH_4^+$, 11); 427 ($L - {}^iPr^+$, 18); 411 ($L - {}^iPr - CH_4^+$, 16); 294 ($L - C_6H_3{}^iPr_2NH^+$, 100); 278 ($L - C_6H_3{}^iPr_2NH - CH_4^+$, 72); 177 ($C_6H_3{}^iPr_2NH_2^+$, 13%).

Preparation of η^6-[$CH_3C(NC_6H_3{}^iPr_2\text{-}2,6)NH(2,6\text{-}^iPr_2C_6H_3)]Mo(CO)_3$ 8c

Prepared from 500 mg of **7c** in a similar manner to **8a**. Reaction stopped after 20 h, after IR indicated that all the intermediate was consumed. On cooling, a black solid was filtered off, and the filtrate cooled to −30 °C. Slightly green-tinted yellow crystals formed, which were filtered and dried under vacuum, yield 571 mg (1.0 mmol, 77%). Recrystallization from 13 mL of *n*-heptane with some Celite (hot-filtered) provided an analytical sample as bright yellow crystals, mp 95 °C (decomp.) (Calc. for $C_{29}H_{38}MoN_2O_3$: C, 62.36; H, 6.86; N, 5.02. Found: C, 62.50; H, 6.92; N, 4.83%). IR: ν(N–H) 3426, 3239, ν(C≡O) 1952, 1871, ν(N–C–N) 1640 cm^{-1}. ^{1}H NMR: δ 7.98 (s, 1 H), 7.35–7.17 (m, 3 H), 5.82–5.58 (m, 3 H), 3.19 (hept, 6.9, 2 H), 2.81 (hept, 6.9, 2 H), 1.79 (s, 3 H), 1.29 (d, 6.9, 6 H), 1.25 (d, 6.9, 6 H), 1.24 (d, 6.9, 6 H), 1.22 (d, 6.9 Hz, 6 H). ^{13}C NMR spectrum not obtained due to sample instability. MS: *m*/*z* 560.19365 (M^+ based on ^{98}Mo, 5); 474 ($M - 3CO, H^+$, 29); 378 (L^+, 20); 335 ($L - {}^iPr^+$, 20); 202 ($L - C_6H_3{}^iPr_2NH^+$, 100); 177 ($C_6H_3{}^iPr_2NH_2^+$, 32%).

Preparation of η^1-[$CH_3C(NC_6H_3{}^iPr_2\text{-}2,6)NH(2,6\text{-}^iPr_2C_6H_3)]Mo(CO)_5$ 9c

500 mg (1.3 mmol) of **7c** and 350 mg (1.3 mmol) of $Mo(CO)_6$ were loaded under N_2 into a Schlenk tube; 27 mL of dry *n*-heptane was then added, and the mixture heated to reflux. Progress of the reaction was monitored by solution IR, and

heating discontinued after 1.5 h. At room temperature, colourless crystals formed (unreacted **7c**), which were filtered off and discarded. Cooling the filtrate to −30 °C produced 380 mg of green-tinted yellow crystals [0.62 mol, 47% yield, mp 125–130 °C (decomp.)]. An analytical sample of pale yellow crystals was obtained by dissolving this material at room temperature in 23 mL of *n*-heptane, and cooling to −30 °C (Calc. for $C_{31}H_{38}MoN_2O_5$: C, 60.58; H, 6.23; N, 4.56. Found: C, 60.99; H, 6.27; N, 4.40%). IR: *ν*(N–H) 3341, *ν*(C=O) 2071, 2000, 1930, *ν*(N–C–N) 1640, 1600, 1579 cm^{-1}. ^1H NMR: *δ* 7.37 (s, 1 H), 7.40–7.16 (m, 6 H), 3.16 (hept, 6.9, 2 H), 3.15 (hept, 6.8, 2 H), 1.42 (s, 3 H), 1.40 (d, 6.9, 6 H), 1.30 (d, 6.8, 6 H), 1.27 (d, 6.9, 6 H), 1.11 (d, 6.8 Hz, 6 H). ^{13}C NMR spectrum not obtained due to sample instability. MS: *m*/*z* 560.19517 ($M - 2CO^+$, 5); 474 ($M - 5CO$, H^+, 29); 378 (L^+, 17); 335 ($L - {}^iPr^+$, 19); 202 ($L - C_6H_3{}^iPr_2NH^+$, 100%).

Crystallography

Details of data collection, crystal parameters, solution and refinement are presented in Table 1. Refinement was on F^2 against *all* reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(*gt*) *etc.* and is not relevant to the choice of reflections for refinement. The hydrogen atoms were refined freely with isotropic thermal parameters; all other atoms were refined anisotropically. For **7a**, a disorder model was refined with a 72 : 28 ratio for the H atoms attached to N(1) and N(2), for which atoms the distances *d*(N–H) were constrained to 0.93 Å. For **7c**, which crystallizes in a chiral space group, no reliable determination of the absolute structure was possible. Selected interatomic distances and angles, including H-bonding, are given in Table 2. PLUTO diagrams were prepared using the version incorporated into NRCVAX.[15]

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See http://www.rsc.org/suppdata/dt/1998/4147/ for crystallographic files in .cif format.

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