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A New, Flexible *N*,*N*,*N*-Tripodal Facially Capping Ligand System: Synthesis and Structural Characterization of β-Triketimines and Their $M(CO)_3$ Complexes (M = Cr, Mo, W)

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Dedicated to the memory of Swiatoslaw (Jerry) Trofimenko[†]

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Reaction of imidoyl chlorides Ar*N=CClR (Ar* = 2-*i*PrC_6H_4, 2,6-*i*Pr$_2C_6H_3$, 2-MeOC_6H_4; R = Me, Ph, *t*Bu) with [Li(nacnac)] [nacnac = (Ar*NCMe)$_2$CH] gives β-triketimines L, most of which exist in solution in equilibrium with their imine/enamine tautomers. The route is highly modular, allowing independent variation of at least five parameters. The solution equilibria are very sensitive to such substituent pattern variation. Single-crystal X-ray diffraction analyses of examples of both tautomers and a geometric isomer in the solid state are presented, alongside solution NMR studies of the tautomerism. All examples revert exclusively to the β-triimine form on complexation with $M(CO)_3$ fragments (M = Cr, Mo, W). Facial isomers result. The ligands are weak σ-donors, as adjudged by CO IR stretching frequencies in [$LM(CO)_3$]. Crystal-structure determination on the isostructural pair [HC(2-*i*PrC_6H_4N=CMe)$_3$M(CO)$_3$] (M = Cr, Mo) revealed a hexagonal packing arrangement composed of aryl–aryl and carbonyl (CO)–H–C interactions which generates pseudocylindrical voids accounting for 6–9 % of the crystal volume. In only one case were these occupied by solvent molecules. This family of facially capping *N*,*N*,*N*-ligands with finely tunable bulk have wide potential in coordination chemistry.

Introduction

The provision of new ligands underpins the development of new coordination chemistry. Illustrating this tenet is the wide array of novel results across main group, organometallic and classical coordination chemistry supported by the bulky β-diketiminate ligand class: since its introduction as a neutral β-diimine in 1997,[1] followed by its more frequent use as an *N*,*N*-bidentate spectator monoanion in 1998,[2] [(2,6-*i*Pr$_2C_6H_3$NCMe)$_2$CH]$^-$ (dipp-nacnac) has become a ligand of choice in generating low-coordination-number complexes.[3] In a recent paper we described some fluorinated examples of this type of anion, and reported the reversible addition of ketones to generate a fragile *N*,*N*,*O*-scorpionate ligand which dissociated upon dissolution or attempted isolation as neutral species.[4] We also reported the *C*-alkylation of the anions to generate neutral β-diimines lacking α-hydrogen acidity.[5] Here, we report the use of more functional electrophiles, imidoyl chlorides, which proceed by elimination of LiCl to yield isolable *tri*dentate proligands, also posessed of the significant and variable *ortho*-bulk that characterized the renaissance of the nacnac ligand class, which we term β-triketimines. The resultant ligands (**i**) merit consideration alongside such well-established ligand classes as "trisox" (**ii**),[6] tris(pyrazolyl)methanes (**iii**),[7] "protach" triimines (**iv**),[8] triazacyclohexanes (**v**),[9] and tris(imidazoles) (**vi**),[10] in applications which include supramolecular, biomimetic and catalytic chemistry (see ref.[6–10] and references therein).

The closest literature precedents to the triketimines L described here concern trialdimines, lacking *ortho* bulk, which have been used only in their anionic form, as bidentate, fluxional ligating species.[11] Relevant precedent exists also in the work of Busch and others, where addition of acetoni-

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trile to macrocyclic N_4-ligands, followed by hydrogen rearrangement, furnished complexes, which could be regarded as aza-cryptand analogues.[12] More recent work has seen this concept applied to open-chain N_4-ligands, with an extended range of nitriles used on a single dipyridyl-substituted β-diketiminate Fe complex.[13] We here demonstrate triketimines as neutral, tridentate facially capping ligands in the products of their reactions with $M(CO)_6$ (M = Cr, Mo, W), report the remarkably flexible and controllable modular synthesis of range of examples varying both diketiminate and imidoyl electrophile, and discuss the imine/enamine tautomerism exhibited by these proligands.

Results and Discussion

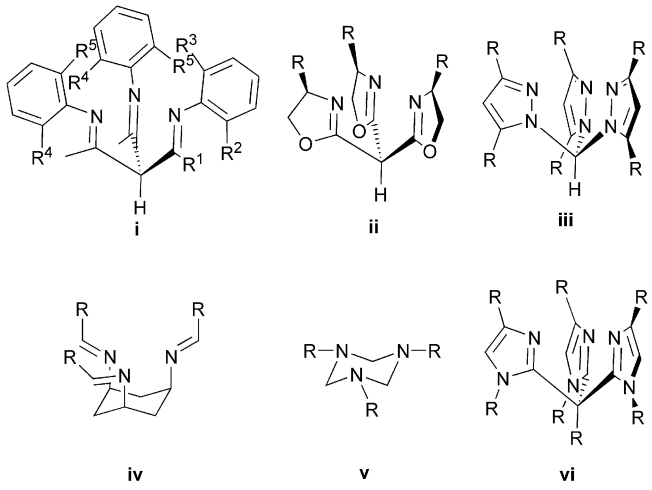
Ligand Synthesis

The parent β-enamine-imines were prepared rapidly in moderate yield by the literature method of acid-catalysed condensation facilitated by toluene/water azeotropic distillation.[2] In the current paper, only examples with identical aniline groups on each arm of the enamine-imine are reported, but the azeotropic distillation technique has previously been used to synthesise from acetylacetone enamine-imines with two different aniline groups present.[14] Furthermore, the lowered symmetry can be achieved in the carbon backbone also, either by starting with a less symmetric diketone, or by using different imidoyl chlorides in the coupling process used to prepare bulkier versions of nacnac.[15] In principle, therefore, the route could offer a total of nine independently variable parameters, giving exquisite control of the ligating pocket dimensions. We restrict ourselves in this first paper to discussion of variation in only 5 of those parameters, as defined in Scheme 1 (**i**). Eleven representative examples of the resultant triketimines are shown in Table 1. These were obtained from reaction of lithiated diketimines with imidoyl chlorides, in turn obtained from amides by chlorination with thionyl chloride, or triphosgene in the case of *N*-acetylanilines. For this case also, in the imidoyl chloride synthesis, the *ortho* bulk on the aniline is necessary to inhibit imidoyl self-condensation;[16] this, coupled with the lower temperature of the triphosgene-mediated synthesis, was found to be advantageous in minimizing this side-reaction. Where the imidoyl substituent R^1 does not posess aza-enolizable protons (as for *N*-pivaloyl- or *N*-benzoylanilines) the choice of aniline substituent is wider, allowing introduction of functional groups such as OMe. The ligand synthesis is shown in full in Scheme 2.

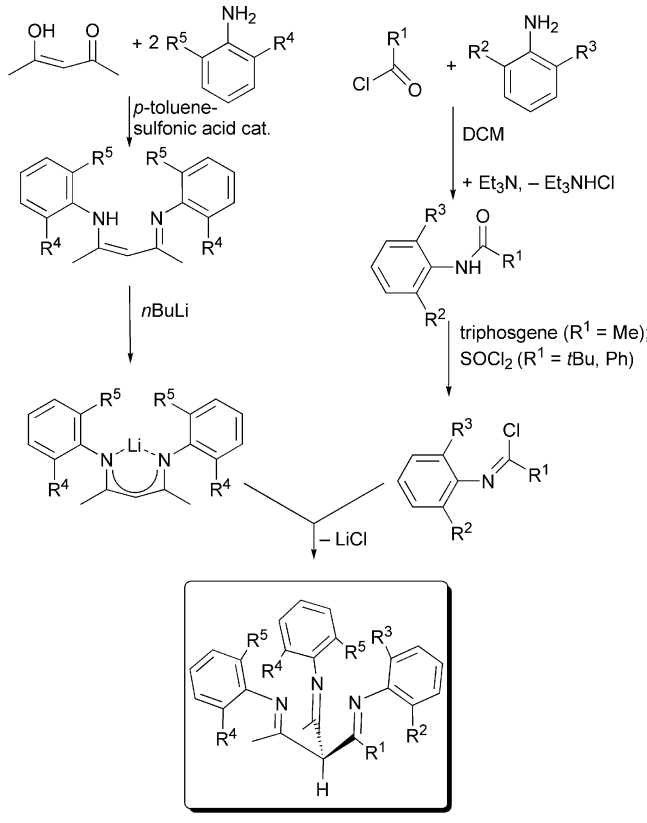
Table 1. Triketimine key.

Triketimine	R^1	R^2	R^3	R^4	R^5
1a	Me	H	*i*Pr	H	*i*Pr
1b	*t*Bu	*i*Pr	*i*Pr	H	*i*Pr
1c	*t*Bu	H	*i*Pr	H	*i*Pr
1d	Me	*i*Pr	*i*Pr	*i*Pr	*i*Pr
1e	Me	H	*t*Bu	H	*i*Pr
1f	Me	*i*Pr	*i*Pr	H	*t*Bu
1g	Me	*i*Pr	*i*Pr	H	*i*Pr
1h[a]	*t*Bu	Me	Me	H	*i*Pr
1i	Me	H	*i*Pr	*i*Pr	*i*Pr
1j	*t*Bu	H	OMe	H	*i*Pr
1k	Ph	H	*i*Pr	H	*i*Pr

[a] *p*-Me in addition to R^2 and R^3 (mesityl).



Scheme 1. Tripodal *N*,*N*,*N*-ligands.

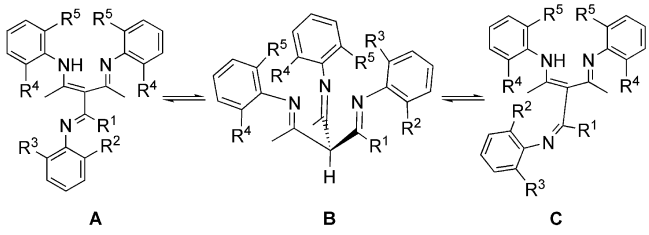


Scheme 2. Overall synthesis of triketimines from commercial reagents.

Addition of the imidoyl chlorides to the lithium diketiminates appears to proceed with good chemoselectivity for C–C bond formation, as was previously found for other electrophiles.[5] The synthesis does not appear to suffer from competing imidoylation at the nitrogen atom, as was found by Knorr in reactions with dialdimines (vinamidines).[11] We ascribe this difference to the protective effect of the *ortho*-aryl substituents in the diketiminates used in this study, though a full analysis of minor byproducts removed by crystallization was not undertaken.

Ligand Solid-State Structures

Three crystal structures of proligands L were obtained, fortuitously, one for each tautomer/isomer believed to exist in solution (vide infra). The three forms are depicted schematically in Scheme 3.



Scheme 3. Tautomer/geometrical isomer equilibria.

Figure 1 shows the solid-state structure of **1a**, potentially the most symmetrical case, but which prefers to crystallise in the enamine-diimine tautomeric form **A** (Scheme 3) which allows the intramolecular N–H–N hydrogen bond found in the starting material to persist.

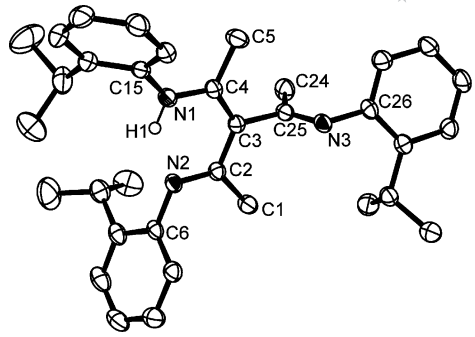


Figure 1. Crystal and molecular structure of **1a**, tautomerizing hydrogen atom shown, others omitted.

The (*E*,*E*,*E*) conformation adopted by **1a** means that 1,3-sigmatropic hydrogen shift is all that is required to generate the tridentate proligand geometry **B**. The alternative enamine-diimine (*E*,*E*,*Z*) geometry **C** was disfavoured because it would render adjacent the two bulkiest substituents about the C(25)–N(3) double bond.

The bond lengths (Table 2) within the enamine-imine H-bonded ring of **1a** are consistent with the alternating single and double bonds of a conjugated system, typical of the parent enamine-imine.[5] The unique imine is isolated by its almost orthogonal angle to the enamine-imine plane, and shows a bond length more typical of an unconjugated imine. At 69°, the angle between the C(6) aryl plane and the imine plane C(1)–C(2)–N(2)–C(3) evidenced minimal conjugation there also, consistent with the short C=N bond [1.277(2) Å].

Table 2. Selected bond lengths [Å] and angles [°] for **1a**–**c**.

1a		**1b**		**1c**	
N(1)–C(4)	1.3584(19)	N(1)–C(10)	1.272(3)	N(1)–C(2)	1.326(2)
N(1)–C(15)	1.417(2)	N(1)–C(1)	1.431(3)	N(1)–C(15)	1.429(2)
N(2)–C(2)	1.3046(18)	N(2)–C(25)	1.276(3)	N(2)–C(4)	1.326(2)
N(2)–C(6)	1.4156(19)	N(2)–C(13)	1.424(3)	N(2)–C(6)	1.426(2)
N(3)–C(25)	1.277(2)	N(3)–C(39)	1.274(3)	N(3)–C(25)	1.286(2)
N(3)–C(26)	1.4270(19)	N(3)–C(30)	1.427(3)	N(3)–C(26)	1.417(2)
C(2)–C(1)	1.507(2)	C(10)–C(11)	1.504(3)	C(1)–C(2)	1.506(3)
C(2)–C(3)	1.450(2)	C(10)–C(12)	1.526(3)	C(3)–C(2)	1.416(2)
C(3)–C(4)	1.379(2)	C(12)–C(39)	1.520(4)	C(3)–C(4)	1.425(3)
C(3)–C(25)	1.512(2)	C(12)–C(25)	1.537(4)	C(3)–C(25)	1.509(3)
C(25)–C(24)	1.508(2)	C(39)–C(40)	1.506(4)	C(25)–C(24)	1.551(3)
C(4)–N(1)–C(15)	127.59(13)	C(10)–N(1)–C(1)	119.8(2)	C(2)–N(1)–C(15)	123.88(17)
C(2)–N(2)–C(6)	121.35(13)	C(25)–N(2)–C(13)	129.2(2)	C(4)–N(2)–C(6)	122.92(16)
C(25)–N(3)–C(26)	121.95(14)	C(39)–N(3)–C(30)	120.4(2)	C(25)–N(3)–C(26)	123.04(15)
N(2)–C(2)–C(3)	120.25(14)	N(1)–C(10)–C(11)	126.6(2)	N(1)–C(2)–C(3)	121.39(17)
N(2)–C(2)–C(1)	122.37(13)	N(1)–C(10)–C(12)	117.7(2)	N(1)–C(2)–C(1)	117.97(16)
C(3)–C(2)–C(1)	117.38(13)	C(11)–C(10)–C(12)	115.6(2)	C(3)–C(2)–C(1)	120.55(16)
C(4)–C(3)–C(2)	123.90(13)	C(39)–C(12)–C(10)	109.0(2)	C(2)–C(3)–C(4)	122.71(17)
C(4)–C(3)–C(25)	117.92(13)	C(39)–C(12)–C(25)	112.7(2)	C(4)–C(3)–C(25)	118.54(15)
C(2)–C(3)–C(25)	118.10(13)	C(10)–C(12)–C(25)	111.2(2)	C(2)–C(3)–C(25)	118.53(16)
N(3)–C(25)–C(24)	125.34(14)	N(2)–C(25)–C(12)	114.4(2)	N(3)–C(25)–C(24)	114.24(16)
N(3)–C(25)–C(3)	117.44(14)	N(2)–C(25)–C(26)	128.3(3)	N(3)–C(25)–C(3)	123.89(16)
C(24)–C(25)–C(3)	117.21(14)	C(12)–C(25)–C(26)	117.1(2)	C(3)–C(25)–C(24)	121.78(15)
N(1)–C(4)–C(3)	120.58(14)	N(3)–C(39)–C(40)	126.5(3)	N(2)–C(4)–C(3)	120.56(16)
C(3)–C(4)–C(5)	121.12(13)	N(3)–C(39)–C(12)	118.6(3)	C(3)–C(4)–C(5)	120.28(16)
N(1)–C(4)–C(5)	118.27(13)	C(40)–C(39)–C(12)	114.9(3)	N(2)–C(4)–C(5)	119.16(16)

For **1b**, in which both 2- and 6-isopropyl groups are present on one aryl group, and where a *tert*-butyl group has replaced methyl substituent R^1 (Figure 2), the true triketimine form **B** was observed, mirroring the behaviour of similarly bulky β-diimines.[17] It seems at first strange that there was no requirement for (*E*) disposition of the *tert*-butyl group and the 2,6-disubstituted aryl group, giving the alternative enamine-diimine form **C**. This was prevented by the unfavourable R^2–C(12) steric repulsion that would result. Consequently, form **B** has a (*Z*) disposition of the *tert*-butyl group and the pendant aryl group, as does form **A**. The strain that this causes in form **B** for **1b** is shown by the C(26)–C(25)–N(2) and C(25)–N(2)–C(13) angles of 128.3 and 129.2°, respectively (Table 2). Mapping of this situation onto form **A** would push R^1 significantly towards fulcrum carbon atom C(12). Hence, it is the avoidance of an induced steric clash, which pushes C(12) away from R^1, and guarantees the sacrifice of the N–H–N hydrogen bond. Consequently, all three imine bonds in **1b** exhibit an (*E*,*E*,*E*) disposition and define an as-yet unfilled pocket. This conformation is perfectly predisposed for coordination: minimal reorganisation is required upon metal binding.

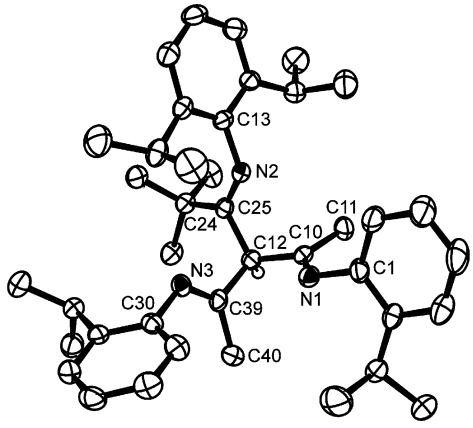


Figure 2. Crystal and molecular structure of **1b**, C(12) hydrogen atom shown, others omitted.

In **1c** (Figure 3), bearing one fewer isopropyl substituent than **1b**, the (*E*) disposition of the pendant imine causes no serious steric clash with the fulcrum carbon atom C(3), and so the N–H–N hydrogen bond and conjugated system of the enamine-imine is regained. In fact, in **1c** the C(2)–C(3) and C(3)–C(4) lengths (Table 2) both lie close to 1.42 Å, the arithmetic mean of the corresponding distances in **1a**, and the C–N and C=N distances are crystallographically indistinguishable. The situation was modelled as a 2-site disorder in N–H hydrogen position, with an implicit (unresolved) 2-site disorder in the positioning of single and double bonds round the enamine-imine, reflecting closely the dynamic solution NMR behaviour. A satisfactory refinement also resulted if the hydrogen atom was left as a single atom, which appeared equidistant between the two nitrogen atoms, which would be consistent with a fully delocalised π-system. We favour the interpretation of the data as disordered.

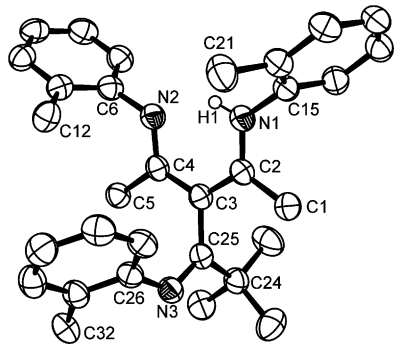


Figure 3. Crystal and molecular structure of **1c**, tautomerizing hydrogen atom shown, others omitted; methyl groups on isopropyl methine atoms C(12), C(21) and C(32) omitted.

In **1a** the plane of the isolated imine lies approximately orthogonal to the plane of the conjugated enamine-imine. In **1c** the angle between these planes is 62.4°. Steric clash of the isopropyl substituent of the isolated arylimine arm [C(32)] and C(5) is prevented by twisting of the aryl plane from orthogonality with the imine plane (twist angle 51.4°): This option is not available to **1b**, because the additional isopropyl group on the aryl group would force orthogonality, making a clash with C(5) and, as previously discussed, with the fulcrum carbon atom [C(3) in the case of **1a** and **1c**, C(12) in the case of **1b**] unavoidable. Consequently, the tris(imine) form is adopted by **1b**, and the aryl groups all lie approximately orthogonal to the imines, whose C=N distances (Table 2) all lie in the range 1.272–1.274 Å.

Tautomerism

The above arguments, giving a molecular structural basis to the preferred isomers/tautomers in the solid state, are potentially open to the criticism that packing forces may be equally important in deciding the observed solid-state structure. However, the NMR spectroscopic data in $CDCl_3$ solution are in persuasive accord with the solid-state results.

For those triketimines with either *t*Bu or Ph at R^1, a single tautomer/isomer was observed in solution. Of these cases, those where the unique imine arm derived from the imidoyl chloride contained a 2,6-disubstituted aryl group ($R^1 \neq$ Me, $R^2 = R^3$: **1b**, **1h**) were composed exclusively of triketimine tautomer **B** in solution, as evidenced by the α-CH singlet at δ = 4–5 ppm, and the absence of the NH signal at δ = 12–15 ppm. Those where the unique aryl group was 2-substituted only ($R^1 \neq$ Me, R^2 = H: **1c**, **1j**, **1k**) were composed exclusively of tautomer/isomer **C** (Scheme 3). The distinction between the (*E*)/(*Z*) isomers **A** and **C** is based upon the assumption that the structure isolated in the solid state is likely to be representative of the single tautomer/isomer observed in solution, and the improbability of an (*E*) geometry in cases where R^1 is larger than Me. There is an alternative hypothesis that the face-strain on the imine bond is increased by the larger substituents, thus lowering the barrier to nitrogen inversion mechanism of

(*E*)/(*Z*) exchange to a point where it is fast at room temperature;[18] however, no evidence was found for such an exchange.

For those triketimines with methyl substituents on each arm (i.e. R^1 = Me: **1a**, **1d**–**1g**, **1i**), a number of exchanging tautomers were observed in solution, i.e. many more peaks than expected for either C_3-symmetric triimine form **B** or enamine-diimine forms **A** and/or **C** (Scheme 3) were observed. However, single-spot TLC and satisfactory elemental analyses attested to the purity of the compounds; cross-peaks between exchanging positions in room-temperature NOESY spectra confirmed that the complexity was the result of a combination of (*Z*)/(*E*) isomerism and imine/enamine tautomerism, i.e. the equilibria shown in Scheme 3, rather than the presence of more than a single compound. In all these cases the dominant form (ca. 50–70%) was **A**, rather than **C**, as shown crystallographically for **1a**. For cases in which R^1 = Me but all three aryl groups were not equivalent, the sterically least demanding aryl group occupied the isolated imine position in the most abundant form of the two isomers of **A** possible.

Interestingly, the (*Z*) form **C** caused slowed rotation of the C–C single bond connecting the pendant imine to the fulcrum carbon atom [e.g. C(3)–C(25) in **1c**]. This was shown by doubling of isopropyl methine and *m*-aryl peaks where a 2,6-*i*$Pr_2C_6H_3$ group occupied an enamine position. In turn, this confirmed slow rotation of the aryl–N bond in those cases.

In all the R^1 = Me cases, a small pair of doublets at δ = 0.9–1.0 ppm was observed, and was assigned to inequivalent methyl groups of isopropyl substituents in the **B** form. The observation of two distinct environments indicated that no molecular plane of symmetry bisected the two methyl groups in any conformation accessible to this tautomer. This indicated that the phenyl groups were essentially fixed on the NMR timescale, precluding even a transient conformation where they shared the imine plane. This was the minor solution tautomer (**1a**, **1e**, **1f**, **1g**, **1i**: ca. 10–20%; **1d**: 50%) in all cases where R^1 = Me. The major tautomer was a mixture of (*E*)/(*Z*) isomers **A** and **C**, with **A** dominant. However, it is clear that for cases where R^1 = Me, the energy differences between these tautomers is slight. It is notable that relatively subtle changes in substituent patterns have such a significant effect on the positions of the equilibria.

In many cases where R^1 = Me but substituent pattern on the three aryl groups varied, this led to an even greater array of conformers/isomers: In **1e**, for example, there are 5 possible isomers/tautomers likely, even neglecting possible *syn*/*anti* isomerism of monosubstituted aryl conformation. Each of these would give rise to multiple isopropyl resonances. It was not always possible to resolve all peaks for all expected isomers, but the observed spectral complexity was consistent with their presence.

It proved possible to monitor exchange of these different tautomers in the simplest case: A solution of **1a** in $(CD_3)_2$-SO showed major changes in the ^{1}H NMR spectrum over the temperature range 25–120 °C. Three processes were observed: The lowest energy of these was aryl–N bond rotation, seen in coalescence of the diastereotopic pair of isopropyl methyl groups in form **B** at approximately 70 °C; **A**/**C** exchange [i.e. (*E*)/(*Z*) isomerism by nitrogen inversion of the pendant imine][18] was observed through coalescence of the backbone methyl groups at approximately 90 °C. Exchange broadening of peaks assigned to triimine tautomer **B** was observed at 120 °C, suggesting commencement of coalescence with the **A**/**C** peaks, indicating equilibration of forms **A**, **B** and **C** by 1,3-prototopic imine/enamine exchange.[19]

Carbonylmetal Complexes

In thermally induced ligand substitution reactions using refluxing dibutyl ether with catalytic thf of **1a**–**1j** with $[M(CO)_6]$ (M = Cr: **2a**–**2j**; M = Mo: **3a**–**3j**; M = W: **4a**) the relative abundance of the different tautomers appears to have little bearing on the result or speed of reaction. In all cases, scorpionate complexes were formed, with loss of 3 mol-equiv. of CO. In line with reports detailing other, similar ligands, yields of *fac*-$[LM(CO)_3]$and reaction speeds were maximum for molybdenum (Cr < Mo >> W).[7,20] In the case of $[W(CO)_6]$, optimal yields, though not in excess of 30%, could be attained by use of trimethylamine *N*-oxide as a CO scavenger.[20] Use of 3 mol-equiv. gave a superior yield in a shorter time.

The purely thermally induced reactions proceed through several colour changes to yield red (Cr), orange (Mo) or crimson (W) complexes. These colours are typical of charge-transfer transitions seen in other similar complexes where the $M(CO)_3$ fragment is presented with tri-*N* ligation.[7,20,21] The tris(chelating) nature of the ligands **1** is clearly important in determining this κ_3 coordination, because for *N*-aryl monoketimines or *N*-aryl monoaldimines, π-coordination of the *N*-aryl group was the favoured mode of binding.[22] The three carbonyl fragments dictate the orientation of the *N*-aryl groups to be pseudo-perpendicular to the imine planes (84.9°), such that they have minimal electronic interaction to influence the UV/Vis spectra of the products, all of which show expected aryl π*←π and imine π*←n transitions in addition to MLCT transitions around 500 nm. However, the complexes where R^1 = Ph (**2k**, **3k**) were notably different, giving very darkly coloured complexes, in which the two MLCT absorptions[21] were red-shifted by 20–70 nm. In all other respects, **2k** and **3k** were essentially identical to the other examples.

In many cases, IR spectroscopy showed three CO stretching vibrations, consistent with the solid-state structure determined for [**1a**·$Cr(CO)_3$], i.e. **2a**, by X-ray crystallography. A C_{3v} structure would give 2 bands, A_1 and E, but here the presence of the isopropyl groups destroys the planes of symmetry, thus splitting the E band into a doublet. This splitting was not resolved in all cases, however.

The mean CO stretching frequency (weighted 2:1 in cases where the E band split was not resolved) of 1819 cm^{-1} was approximately 15 cm^{-1} higher than in analogous complexes of tris(pyrazolyl)methanes.[7] This would suggest that the

triketimines **1** are slightly weaker σ-donors than the tris-(pyrazolyl)methanes. The mean frequency varied little over **1a**–**1k** for a given metal. It would appear that the *ortho*-MeO substituent of **1j** was prevented from influencing the donicity of the ligand by the orthogonality of the aryl group with the imine plane. Similarly, varying the ketimine carbon substituent R^1 (Me, *t*Bu, Ph), or varying the metal from Cr to Mo to W, had negligible electronic effect, as adjudged from carbonyl stretching frequencies.

Three isopropyl groups, one on each aryl group, appears to be the optimum fit. In bulkier cases, such as **1f** in which an *o*-*t*Bu group was present on two aryl groups, and 2,6-diisopropyl substitution on the remaining one, reactions were sluggish, and yields and stabilities were low. For **1d**, with 2,6-diisopropyl substituents on all three aryl groups, the reaction failed to proceed at all. On inspection of the crystal structures of **1a**·$Cr(CO)_3$ and **1a**·$Mo(CO)_3$, **2a** and **3a**, respectively, it becomes clear that increased bulk would be difficult to accommodate without causing severe steric clashes around the 6-coordinate metal centre.

Figure 4 depicts the crystal and molecular structure of **2a**. That of **3a** is identical, but for small changes in lattice parameters. Selected bond lengths and angles for each are listed in Table 3. The pair are isostructural and isotypic (see Table 4 for lattice parameters). The asymmetric unit comprises a single imine arm and carbonyl group; a crystallographic axis passes through Cr(1) and C(1), rendering the molecule rigorously C_3-symmetric. The splayed aryl groups result in an inefficient packing of the molecules in their $P\bar{3}c1$ space group. This packing motif and space group clearly have their seed in the inherent threefold point symmetry of the molecule, which results in generation of significant pores along the *c*-axis (Figure 5). The pore volumes of 219 $Å^3$ for **2a**, 311 $Å^3$ for **3a** after removal of solvent,[23] are of the order of the smaller pores in an aluminium trimesate crystal.[24] It, however, was a true 3-dimensional coordination polymer, rather than a molecular crystal. In the case of carbonylmetal complexes, larger hexagonal pores have recently been found, though these are solvent-filled, and from a kinetic product; the crystals do not survive desolvation in the same form.[25] The percentage solvent-accessible volume figures[23] for **2a** (6.5%) and **3a** (8.8%) are modest in comparison, though crystals of **2a** and **3a** are distinguished from the larger-pore compounds by their capacity to retain crystallinity upon solvent loss by evacuation.

The effect of replacing Cr with Mo is seen in the larger cell constants (Table 4) of **3a** versus **2a**. The larger atomic radius of Mo over that of Cr is accommodated by an expansion of the ligand pocket, as judged by the N–N distance in the Mo case of 2.927 Å versus 2.834 Å in the Cr case. This expansion allows the C=N–metal angle to remain close to the sp^2 ideal (M = Cr: 120.73°; M = Mo: 120.85°). It also can account for a lengthening of the *a*/*b* cell dimension of 0.215 Å. The observed lengthening of 0.293 Å results from a combination of this effect with that of the inclusion of a molecule of solvent in the pores of **3a**, where those of **2a** were vacant.

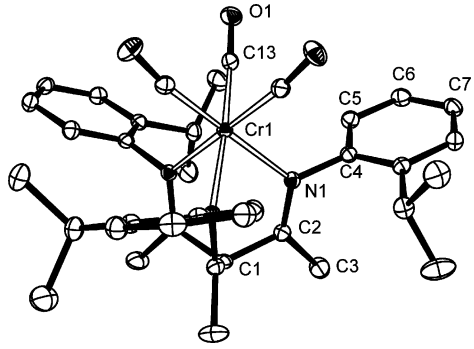


Figure 4. Crystal and molecular structure of **2a**, hydrogen atoms omitted. Compound **3a** is isostructural.

Table 3. Selected bond lengths [Å] and angles [°] for **2a** and **3a**.[a]

2a		**3a**	
Cr(1)–C(13)	1.8336(12)	Mo(1)–C(13)	1.9434(19)
Cr(1)–N(1)	2.1218(10)	Mo(1)–N(1)	2.2599(16)
O(1)–C(13)	1.1673(15)	O(1)–C(13)	1.170(2)
N(1)–C(2)	1.2804(15)	N(1)–C(10)	1.287(2)
N(1)–C(4)	1.4460(14)	N(1)–C(1)	1.448(2)
C(1)–C(2)	1.5211(13)	C(10)–C(11)	1.521(2)
C(2)–C(3)	1.4949(17)	C(10)–C(12)	1.494(3)
C(13)–Cr(1)–C(13)#	183.46(6)	C(13)–Mo(1)–C(13)#1	84.19(9)
C(13)–Cr(1)–N(1)#1	93.99(4)	N(1)–Mo(1)–C(13)#1	95.51(8)
C(13)–Cr(1)–N(1)	98.87(4)	N(1)–Mo(1)–C(13)#2	99.65(8)
C(13)–Cr(1)–N(1)#2	176.36(4)	N(1)–Mo(1)–C(13)	176.11(8)
N(1)–Cr(1)–N(1)#1	83.81(4)	N(1)–Mo(1)–N1#1	80.71(6)
C(2)–N(1)–C(4)	117.83(9)	C(1)–N(1)–C(10)	118.34(16)
C(2)–N(1)–Cr(1)	120.73(8)	Mo(1)–N(1)–C(10)	120.81(13)
C(4)–N(1)–Cr(1)	121.43(7)	Mo(1)–N(1)–C(1)	120.85(11)
C(2)#1–C(1)–C(2)	110.38(8)	C(10)–C(11)–C(10)#1	111.44(15)
N(1)–C(2)–C(3)	127.33(11)	N(1)–C(10)–C(12)	126.10(19)
N(1)–C(2)–C(1)	117.18(12)	N(1)–C(10)–C(11)	117.98(19)
C(3)–C(2)–C(1)	115.47(12)	C(11)–C(10)–C(12)	115.90(17)
O(1)–C(13)–Cr(1)	172.10(11)	Mo(1)–C(13)–O(1)	175.07(16)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-y + 1$, $x - y$, z; #2: $-x + y + 1$, $-x + 1$, z.

The high melting point (neither compound melts, but both decompose at elevated temperaures), and rather poor solubility of **2a** and **3a** suggested that the solid lattice is robust. An analysis of close contacts revealed that two distinct intermolecular interactions may have been responsible: C–H···OC hydrogen bonds, and aryl–aryl interactions. Taking the first of these, the seminal work of Braga and Desiraju gave ranges of the C···O distance from 3.25 up to 4.00 Å as possibly indicating such a hydrogen bond,[26] but that a CH···O angle close to 140° was a superior indicator of such interactions having a structure-directing influence. In both these respects, values for **2a** (3.41 Å and 146.8°, respectively, by using a corrected C–H distance of 1.08 Å, as in the original paper[26]) seem to support this view. Indeed, the corrected H···O distance of 2.45 Å lies within the most populated range of the observed distribution of distances.[26] Less consistent with the view of the interaction as structure-directing is the CO–H angle, which at 94.87° (corrected), is some way sharper than the mean (127.1°) previously recorded for terminal carbonyl groups. It is possible that packing is more strongly dictated by the short

Table 4. X-ray data collection and refinement details.

	1a	**1b**	**1c**	**2a**	**3a**·0.39Et_2O
Empirical formula	$C_{34}H_{43}N_3$	$C_{40}H_{55}N_3$	$C_{37}H_{49}N_3$	$C_{37}H_{43}CrN_3O_3$	$C_{39.57}H_{43}MoN_3O_{3.39}$
M_w	493.71	577.87	535.79	629.74	698.83
Crystal system	monoclinic	monoclinic	monoclinic	rhombohedral	rhombohedral
a [Å]	13.7441(2)	9.7230(3)	9.8756(2)	14.5311(4)	14.8240(4)
b [Å]	10.8258(2)	15.1749(4)	19.9334(4)	14.5311(4)	14.8240(5)
c [Å]	20.3707(4)	24.1171(8)	17.1360(4)	18.4788(10)	18.5430(4)
α [°]	90	90	90	90	90
β [°]	102.6210(10)	90.548(1)	104.9990(10)	90	90
γ [°]	90	90	90	120	120
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{3}c1$	$P\bar{3}c1$
Z	4	4	4	4	4
T [K]	123(2)	123(2)	150(2)	120(2)	200(2)
μ [mm^{-1}]	0.064	0.062	0.063	0.315	0.41
Reflections measured	7205	10910	40515	25211	4602
Reflections observed[a] (R_{int})	7205 (0)	5590 (0.1106)	5711 (0.0655)	3416 (0.0848)	2450(0.0365)
R_1(observed)	0.0508	0.0573	0.0589	0.0445	0.0395
wR_2(all data)[b]	0.1882	0.1297	0.1696	0.1217	0.0882
Device	Kappa CCD	Kappa CCD	Kappa CCD	Synchrotron	Kappa CCD

[a] $I > 2\sigma(I)$. [b] $wR_2 = \{\sigma[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]\}^{1/2}$.

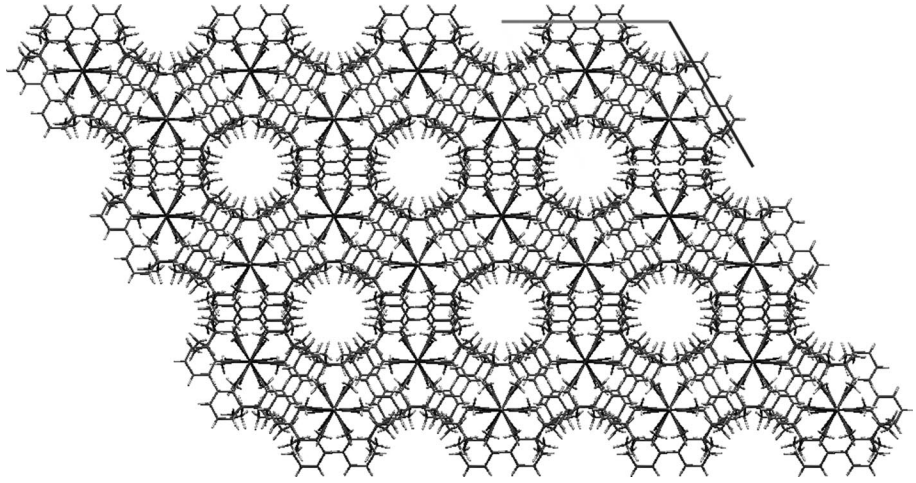


Figure 5. Crystal packing diagram of **3a**, viewed along the *c*-axis, with disordered solvent occupying the pores omitted.

aryl–aryl interactions shown by C(6)–C(6′) and C(7)–C(7′) contacts of 3.37 and 3.38 Å, respectively.[27] The two phenyl rings define mutually parallel planes. These distances and geometry characterise quite strong parallel-slipped aryl interactions. The degree of slippage is so large that it would be incorrect to term it π–π interaction.[25] According to Hunter and Sanders' "rule 3", the interaction is principally a σ–π one.[28] The combination of these two interactions for two asymmetric units from different molecules is shown in Figure 6.

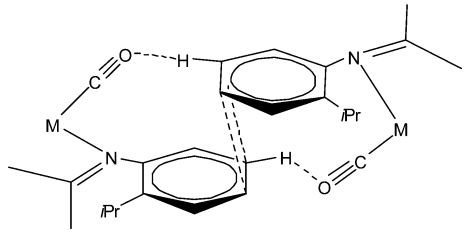


Figure 6. Sketch of supramolecular interactions between two asymmetric units of **2a/3a**.

Because there are three asymmetric units per molecule, crystal symmetry generates an intricate 2D supramolecular network composed of a double-layer of molecules in the *ab*-plane which, though composed of interactions which are individually relatively weak, produce a robust lattice through cooperativity.[29] In **3a**, the aryl σ–π interactions are stretched by the larger radius of Mo, distances of 3.419 and 3.434 Å being less convincing as structure-directing elements. However, the O···H distance is a full 0.1 Å longer than in **2**a, so both intermolecular contacts must be deemed weaker. Interestingly, **2g** and **3g**, with a single additional isopropyl substituent precluding the supramolecular network, were significantly more soluble than **2a** and **3a**.

For both **2a** and **3a**, NMR spectra in dimethyl sulfoxide solution were consistent with the retention of the C_3 solid-state molecular structures. Two isopropyl methyl resonances confirmed that rotation around the aryl C–N bonds was slow, and hence that the solutions were racemic mixtures of enantiomers.Very small peaks in some cases of **2** and

3 evidenced minor contributions from alternative rotamers placing 2-substituents from adjacent rings close to each other, suggesting that some slow interconversion was possible, but attempts to monitor this process at raised temperatures were thwarted by sample decomposition. Lower-symmetry cases also showed the effects of "fixed" *N*–aryl bonds; for example in **3c**, where the C_3 symmetry element is destroyed by the presence of an R^1 = *t*Bu group, separate signals were observed for each of the *six* distinct methyl isopropyl groups, indicating a C_1 symmetry in solution on the NMR timescale.

Given the robust lattice of **2a**, an attempt was made to track structural changes resulting from pumping of the MLCT electronic transitions with constant 532 nm laser irradiation, while diffraction data were recorded. Whereas none were detected, the overnight exposure of a crystal of **2a** to a stream of nitrogen gas at –120 °C caused an increase in residual electron density in the pores, corresponding to approximately 20% of a nitrogen molecule, despite the perfluoro(polyether) oil coating of the crystal. This observation prompted a study of the gas adsorption properties of **2a** and **3a**, the results of which will be subject to a future publication. Reports of coordination and catalytic chemistry with oxidised metal ions, and introduction of further functionality to positions R^2 and R^3 directed at the obvious biomimetic applications of the new ligand system, shall also be forthcoming.

Conclusions

A range of examples of the new triketimine proligand class L are presented, demonstrating the convenient modularity and flexibility of synthesis, which makes fine control of the dimensions and shape of the ligating pocket possible. Solution equilibria [(*E*)/(*Z*) and imine/enamine] are strongly dependent on substitution patterns, but have little effect on behaviour of the species as ligands.

The behaviour of the triketimines as facially capping tridentate neutral ligands, complementing such well-established ligand classes as tris(pyrazolyl)methanes, etc. was demonstrated in $[LM(CO)_3]$ (M = Cr, Mo, W). A limit to the degree of *ortho* bulk tolerated in such six-coordinate complexes was found. Where each imine-aryl group was 2-substituted by a single isopropyl group, crystalline compounds were obtained. Rigorous crystallographic C_3 symmetry was imposed, and a combination of aryl–aryl and C–H···OC interactions built a 2D network of a double-layer of molecules in the *ab*-plane with pores along the *c*-axis, occupied by solvent in the case of **3a**, but vacant in **2a**. This C_3-symmetrical conformation was retained in solution. Spectroscopically, only minor differences were noted with varying substituent patterns in complexes, but we expect more striking variation in forthcoming catalysis studies.

Experimental Section

General: Anilines, amines and chlorinated solvents were distilled from calcium hydride. Toluene, diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl, hexane from sodium/benzophenenone ketyl with 5% added tetraglyme. The following compounds were synthesised according to literature procedures: enamine-imines 2,6-*i*$Pr_2C_6H_3$NHCMeCHCMeN-2,6-*i*$Pr_2C_6H_3$ (CAS reference 181708-81-6),[2] 2-*i*PrC_6H_4NHCMeCHCMeN-2-*i*PrC_6H_4 (368891-65-0),[5] 2-*t*BuC_6H_4NHCMeCHCMeN-2-*t*BuC_6H_4 (213275-19-5),[30] 2-$MeOC_6H_4$NHCMeCHCMeN-2-$MeOC_6H_4$ (613685-98-6);[5] amides *t*BuCONH-2-*i*PrC_6H_4 (33768-49-9),[30] *t*BuCONH-2-$MeOC_6H_4$ (33768-49-9),[31] MeCONH-2-*i*PrC_6H_4 (19246-04-9),[32] PhCONH-2-*i*PrC_6H_4,(93007-80-8)[32] MeCONH-2,6-*i*$Pr_2C_6H_3$ (116637-13-1),[33] MeCONH-2-*t*BuC_6H_4 (7402-70-2);[32] *t*BuCONH-2,4,6-$Me_3C_6H_2$ (19699-10-6)[34] and *t*BuCONH-2,6-*i*$Pr_2C_6H_3$ (215715-81-4);[15] imidoyl chlorides MeC(Cl)=N-2,6-*i*$Pr_2C_6H_3$ (304865-77-8),[35] *t*BuC(Cl)=N-2,4,6-$Me_3C_6H_2$ (2085-36-8)[15] and *t*BuC(Cl)=N-2,6-*i*$Pr_2C_6H_3$ (215715-82-5).[15] Other materials were purchased from commercial vendors and used as received. All manipulations except the workup of the ligand syntheses and characterization of ligands and complexes were performed under argon by using argon/vacuum double manifold or argon-filled recirculating glovebox equipped with internally mounted moisture- and oxygen-scrubbing columns. Details of NMR spectroscopic equipment and referencing procedures are as described elsewhere.[5] Assignments were confirmed by appropriate COSY, HMQC, DEPT and NOESY experiments. In all cases, where coupling constants are not stated, it is because chemically reasonable, reproducible and self-consistent values were not extractable from the data, which in most cases was suffering from serious overlap. Microanalyses were obtained from the University of Manchester School of Chemistry Microanalysis Service.

Imidoyl Chlorides

MeC(Cl)=N-2-*i*PrC_6H_4: In a round-bottomed flask equipped with a reflux condenser, triphosgene (16.51 g, 0.0556 mol; ***CAUTION:*** lachrymator, may liberate phosgene under heating) was added portionwise by means of a solids addition tube to a magnetically stirred solution of amide MeCONH-2-*i*PrC_6H_4 (29 g, 0.164 mol) in dichloromethane (100 mL) at 0 °C. The colourless solution was stirred for 30 min then heated to reflux for 4 h, and stirred at room temperature overnight. Liberated HCl was scrubbed from the protective nitrogen stream with an aqueous NaOH absorption tower before being discharged to the fumehood. Distillation under vacuum (0.01 Torr) gave **3a** as a colourless liquid at 72–76 °C (23.3 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 [d, $^3J_{HH}$ = 4.5 Hz, 6 H, $CH(CH_3)_2$], 2.68 (s, 3 H, CH_3), 2.98 (sept, $^3J_{HH}$ = 6 Hz, 1 H, *i*Pr C*H*), 6.75–7.38 (aromatic protons, 4 H) ppm. $^{13}C\{^1H\}$ NMR (100.57 MHz, $CDCl_3$): δ = 23.5 [s, $(CH_3)_2CH$], 28.8 [s, $(CH_3)_2CH$], 30.2 [s, $N=C(Cl)CH_3$], 120.3, 125.7, 126.1, 126.5 (4 s, aryl *C*H), 139.0 (s, aryl *C*–*i*Pr), 143.2 [$N=C(Cl)CH_3$], 145.6 (s, aryl *C*–N) ppm. IR (thin film on NaCl plates): $\tilde{\nu}$ = 1708 [ν(C=N)] cm^{-1}. The crude, air-sensitive oil was used in subsequent transformations without further characterisation.

MeC(Cl)=N-2-*t*BuC_6H_4: Prepared in an analogous way to that described above, from amide MeCONH-2-*t*BuC_6H_4, to yield a colourless oil distilling at 84–92 °C (0.01 Torr) (4.97 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (s, 9 H, *t*Bu CH_3), 2.25 (s, 3 H, CH_3), 7.20–7.65 (4 H, aromatic protons) ppm.

***t*BuC(Cl)=N-2-$MeOC_6H_4$:** Amide *t*BuCONH-2-$MeOC_6H_4$ (26.0 g, 0.126 mol) was dissolved in $SOCl_2$ (36 mL, 0.493 mol) to give an orange solution, which was heated under reflux for 2 h. Excess thionyl chloride was removed by distillation under argon. Vaccum distillation (80–84 °C, 0.01 Torr) gave *t*BuC(Cl)=N-2-$MeOC_6H_4$ as a bright yellow oil (26.82 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ

= 1.40 (s, 9 H, *t*Bu CH_3), 3.85 (s, 3 H, OCH_3), 6.75–7.15 (4 H, aromatic protons) ppm.

***t*BuC(Cl)=N-2-*i*PrC$_6$H$_4$:** Prepared in an analogous way to that described above, from amide MeCONH-2-*i*PrC$_6$H$_4$ (28.5 g, 0.130 mol) and $SOCl_2$ (100 mL) to yield a yellow oil distilling at 130 °C (0.01 Torr) (24.90 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (d, $^3J_{HH}$ = 7.5 Hz, 6 H, *i*Pr CH_3), 1.33 (s, 9 H, *t*Bu CH_3), 2.83 (sept, $^3J_{HH}$ = 7.5 Hz, ^{1}H, *i*Pr C*H*), 6.60–7.30 (non-first-order m, 4 H, aromatic protons) ppm.

PhC(Cl)=N-2-*i*PrC$_6$H$_4$: Prepared in an analogous way to that described above, from amide PhCONH-2-*i*PrC$_6$H$_4$ (20.02 g, 0.084 mol) and $SOCl_2$ (92 mL) to yield a yellow oil distilling at 122 °C (0.01 Torr) (15.10 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, $^3J_{HH}$ = 7.5 Hz, 6 H, *i*Pr CH_3), 2.96 (sept, $^3J_{HH}$ = 7.5 Hz, 1 H, *i*Pr C*H*), 6.70–7.50 (non-first-order m, 8 H, aromatic protons), 8.12 (d, $^3J_{HH}$ = 7.5 Hz, 1 H) ppm.

Triketimine Proligands: All triketimines were synthesised in a similar manner. Full details are given for **1a**, outline data for other cases.

1a: In a typical procedure, a suspension of 2-*i*PrC$_6$H$_4$NHCMeCHCMeN-2-*i*PrC$_6$H$_4$ (17.10 g, 0.0512 mol) in *n*-hexane (100 mL) was treated with *n*-butyllithium (32.0 mL of a 1.6 M solution in hexanes, 0.0512 mol) at 0 °C, forming a dark yellow solution. This was stirred at 0 °C for 30 min, after which time MeC(Cl)=N-2-*i*PrC$_6$H$_4$ (10.0 mL, 0.0512 mol) was added, immediately causing the formation of a yellow precipitate. The mixture was warmed to room temperature and stirred overnight. The voluminous yellow mixture was poured into water (200 mL), and extracted with diethyl ether. The organic phase was separated, and the aqueous phase was further extracted with diethyl ether (3 × 200 mL). The combined organic layers were washed with water (200 mL), dried with $MgSO_4$, filtered and stripped of solvent under vacuum. The crude product was triturated with a small amount of methanol, filtered and washed with cold methanol. Recrystallisation from methanol gave **1a** as a pale yellow crystalline material (16.63 g, 66%); m.p. 130–132 °C. ^{1}H NMR (500 MHz, $CDCl_3$), triimine tautomer (ca. 10%; reported integrals normalised): δ = 0.93, 0.96 [2 d, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$, 18 H], 1.69 (s, 9 H, CH_3CN), 2.70 [sept, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$, 3 H], 4.59 (s, 1 H, α-C*H*), 6.69 (dd, 3 H, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.8 Hz, 3 H, *o*-aryl); enamine-diimine tautomer (major geometric isomer, ca. 80%, reported integrals normalised): δ = 1.07 [d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$], 1.11 [d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH(CH_3)$_2$], 1.97 (s, 6 H, CH_3CN), 2.02 (s, 3 H, CH_3C=N), 3.03 [sept, $^3J_{HH}$ = 7.0 Hz, 1 H, C*H*-(CH$_3$)$_2$], 3.13 [sept $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 6.54 (dd, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.5 Hz, 1 H, Ar^{iPr} *o*-C*H*), 6.83 (dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.6 Hz, 2 H, Ar^{iPr} *o*-C*H*), 7.0–7.1 (complex m, 4 t overlapped, 6 H, *m*- and *p*-aryl C*H*), 7.20 (dd, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.0 Hz, , 2 H, aryl *m*′-C*H*), 7.25 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.0 Hz, 1 H, aryl *m*′-C*H*) 13.57 (br. s, 1 H, N*H*), enamine-diimine tautomer (minor geometric isomer, ca. 10%, reported integrals normalised): δ = 1.07, 1.11 [2 d overlapped with peaks due to major isomer, 18 H, CH(CH_3)$_2$], 1.93 (s, 3 H, CH_3CN), 2.45 (s, 6 H, CH_3CN), 3.02 [sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.26 [sept $^3J_{HH}$ = 6.9 Hz, 1 H, C*H*-(CH$_3$)$_2$], 6.56 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.4 Hz, 2 H, *o*-aryl), 6.52, (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.1 Hz, 1 H, *o*-aryl), 13.30 (br. s, 1 H, N*H*), 6.68–6.69 (non-first-order m), 6.83 (dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1 Hz), 6.94–7.09 (non-first-order m), 7.12–7.15 (non-first-order m), 7.18–7.25 (non-first-order m) ppm. Other minor isomer/tautomer aryl CH peaks overlapped with major isomer, in range δ = 6.94–7.24 ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), triimine tautomer: δ = 19.03 (*C*H$_3$CN), 23.15, 23.19 [CH(*C*H$_3$)$_2$], 27.88 [*C*H(CH$_3$)$_2$] ppm; enamine-diimine tautomer (major geometric isomer): δ = 18.68 (2 *C*H$_3$CN), 24.51 (1 *C*H$_3$CN), 23.34, 23.62 [CH(*C*H$_3$)$_2$], 27.81 [1 *C*H(CH$_3$)$_2$], 28.11 [2 *C*H(CH$_3$)$_2$], 110.44 (alkenyl α-*C*) ppm; enamine-diimine tautomer (minor geometric isomer): δ = 20.41 (1 *C*H$_3$CN), 21.28 (2 *C*H$_3$CN), 23.06, 23.46 [CH(*C*H$_3$)$_2$], 27.44, 27.92 [*C*H(CH$_3$)$_2$], 105.58 (alkenyl α-*C*) ppm; peaks due to aromatic CH for all isomeric species: δ = 118.29, 118.58, 119.68, 123.84, 123.98, 124.14. 124.20, 124.57, 124.61, 124.80, 125.02, 125.45, 125.56, 125.70, 125.74, 125.81, 125.91, 125.95, 126.13, 126.23 ppm; peaks due to aromatic *ipso*-*C*N and -*Ci*Pr for all isomeric species: δ = 138.47, 141.29, 141.80, 141.84, 142.47, 142.65, 146.58, 148.74 ppm; peaks due to conjugated C=N for all species: δ = 157.81, 158.17 ppm; peaks due to isolated C=N/triimine C=N for all species: δ = 169.95, 171.96 ppm. $C_{34}H_{43}N_3$ (493.73): calcd. C 82.71, H 8.78, N 8.51; found C 82.75, H 9.01, N 8.46. MS (ES$^+$): *m*/*z* = 494.4 [MH]$^+$. IR: $\tilde{\nu}$ = 1643, 1610, 1593, 1573 [ν(C=N)] 1537 [ν(C=C), aromatic] cm^{-1}.

1b: Synthesised as above; 2-*i*PrC$_6$H$_4$NHCMeCHCMeN-2-*i*PrC$_6$H$_4$ (10 g, 0.0299 mol), *n*BuLi (19.5 mL of a 1.6 M hexane solution, 0.0312 mol), *t*BuC(Cl)=N-2,6-*i*Pr$_2$C$_6$H$_3$ (8.6 mL, 0.0308 mol) and hexane (70 mL) were used. Large colourless crystals from methanol/dichloromethane (11.96 g, 70%); m.p. 123–126 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (d, $^3J_{HH}$ = 6.5 Hz, 6 H), 1.02 (d, $^3J_{HH}$ = 6.9 Hz, 6 H), 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 6 H), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$], 1.15 [s, 9 H, *t*Bu C(CH_3)$_3$], 1.92 (s, 6 H, CH_3CN), 2.97–2.98 [2 overlapping sept, $^3J_{HH}$ = 6.5 and 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$], 4.90 (br. s, 1 H, α-C*H*), 6.48 (dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3 Hz, 2 H, Ar^{iPr} *o*-C*H*), 6.88 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar^{iPr2} *p*-C*H*), 6.96 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, Ar^{iPr2} *m*-C*H*), overlapped with 6.97 (td, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.2 Hz, 2 H, Ar^{iPr} *p*-C*H*), 7.03 (td, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5 Hz, 2 H, Ar^{iPr} *m*-C*H*), 7.19 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz, 2 H, Ar^{iPr} *m*′-C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.61 (*C*H$_3$CN), 22.04, 23.26, 24.44 [3 CH(*C*H$_3$)$_2$], 27.68, 28.11 [*i*Pr *C*H(CH$_3$)$_2$], 29.04 [*t*Bu C(*C*H$_3$)$_3$], 44.20 [*t*Bu *C*(CH$_3$)$_3$], 68.11 (α-*C*H), 118.38 (Ar^{iPr} *o*-*C*H), 122.21 (Ar^{iPr2} *m*′-*C*H), 122.38 (Ar^{iPr2} *m*-*C*H), 123.60 (Ar^{iPr} *p*-*C*H), 125.50 (Ar^{iPr} *m*′-*C*H) 126.05 (Ar^{iPr} *m*-*C*H), 134.04, 138.00 (aromatic *ipso*-*Ci*Pr), 146.23, 148.71 (aromatic *ipso*-*C*N), 169.58 (*C*=N) ppm. $C_{40}H_{55}N_3$ (577.89): calcd. C 83.14, H 9.59, N 7.27; found C 83.55, H 9.87, N 7.26. MS (ES$^+$): *m*/*z* = 578.3 [MH]$^+$. IR: $\tilde{\nu}$ = 1663, 1656 [ν(C=N)] 1591, 1574 [ν(C=C), aromatic] cm^{-1}.

1c: 2-*i*PrC$_6$H$_4$NHCMeCHCMeN-2-*i*PrC$_6$H$_4$ (10.15 g, 0.0304 mol), *n*BuLi (19.25 mL of a 1.6 M hexane solution, 0.0308 mol), *t*BuC(Cl)=N-2-*i*PrC$_6$H$_4$ (7.10 mL, 0.0300 mol) and hexane (80 mL) were used. Yellow crystals from MeOH (9.41 g, 59%); m.p. 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (d, $^3J_{HH}$ = 6.9 Hz, 6 H), 0.99 (d, $^3J_{HH}$ = 6.9 Hz, 6 H), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$], 1.34 [s, 9 H, *t*Bu C(CH_3)$_3$], 1.63 (s, 6 H, CH_3CN), 2.81 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H), 3.26 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.60 (dd, 1 H, distorted by non-first-order effects, *o*-CH), 6.65 (dd, $^3J_{HH}$ = 6.9, $^4J_{HH}$ = 2.3 Hz, 2 H, *o*-C*H*), 6.95–7.02 (4 t, 6 H, overlapped, aromatic *m*- and *p*-C*H*), 7.11–7.17 (2 dd, 3 H, distorted by non-first-order effects, *m*′-C*H*), 13.49 (br. s, N*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.60 (*C*H$_3$CN), 22.98, 23.12, 23.30 [CH(*C*H$_3$)$_2$], 27.79 [1 *C*H(CH$_3$)$_2$], 27.96 [2 *C*H-(CH$_3$)$_2$], 30.57 [C(*C*H$_3$)$_3$], 43.00 [*C*(CH$_3$)$_3$], 103.79 (alkenyl α-*C*), 118.64, 124.38, 124.72, 125.07, 125.20, 125.76, 125.94 (aromatic *C*H), 141.51, 141.83, 142.77, 146.91 (aromatic *ipso*-*C*N and -*Ci*Pr), 158.57 (conjugated *C*=N), 179.34 (isolated *C*=N) ppm. $C_{37}H_{49}N_3$ (535.81): calcd. C 82.94, H 9.22, N 7.84; found C 83.89, H 9.18, N 7.93. MS (ES$^+$) *m*/*z*: 536.4 [MH]$^+$. IR: $\tilde{\nu}$ = 1604, 1589, 1558 [ν(C=N)] 1527 [ν(C=C), aromatic] cm^{-1}.

1d: 2,6-*i*Pr$_2$C$_6$H$_3$NHCMeCHCMeN-2,6-*i*Pr$_2$C$_6$H$_3$ (4.2 g, 0.01 mol), *n*BuLi (6.3 mL of a 1.6 M hexane solution, 0.01 mol) and MeC(Cl)=N-2,6-*i*Pr$_2$C$_6$H$_3$ (2.5 mL, 0.01 mol) were used. Pale-green crystals from methanol/dichloromethane (2.90 g, 47%); m.p. 166–168 °C. ^{1}H NMR (500 MHz, $CDCl_3$) triketimine tautomer (50%, reported integrals are normalised): δ = 1.02 [d, $^3J_{HH}$ = 6.7 Hz, 18 H, CH(CH_3)$_2$], 1.14 [d, $^3J_{HH}$ = 6.8 Hz, 18 H, CH(CH_3)$_2$], 1.89 (s, 9 H, CH_3CN), 2.95 [sept, overlapped with unique imine arm of enamine-diimine, $^3J_{HH}$ = 6.8 Hz, 6 H, C*H*(CH$_3$)$_2$], 4.74 (s, 1 H, α-C*H*) ppm; enamine-diimine tautomer (50%, reported integrals are normalised): δ = 1.04 [d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$], 1.05 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$], 1.06 [d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(CH_3)$_2$], 1.08 [d, 7.1 Hz, 6 H, CH(CH_3)$_2$], 1.86 (s, 6 H, CH_3CN), 1.93 (s, 3 H, CH_3CN), 2.95 [m, overlapped with triketimine, $^3J_{HH}$ = 7.1 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.08 [sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$], 13.5 (br. s, 1 H, N*H*) ppm; peaks due to aromatic protons for both isomeric species (9 H): δ = 6.97–7.07 (non-first-order m) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), peaks due to both isomeric species (unless otherwise specified): δ = 19.03 [2 *C*H$_3$C(N), enamine-diimine tautomer], 21.59 [*C*H$_3$C(N), triimine tautomer], 23.26, 23.34, 23.74, 23.83, 23.96, 24.36 [*i*Pr CH(*C*H$_3$)$_2$], 25.27 [1 *C*H$_3$C(N), enamine-diimine tautomer], 27.75, 27.84, 28.31 (*i*Pr *C*H(CH$_3$)$_2$], 72.06 (α-*C*H, triimine tautomer), 108.68 (alkenyl α-*C*, enamine-diimine tautomer), 122.96, 123.26, 123.34, 123.59, 123.79,123.35 (aromatic *C*H), 136.55, 136.87, 140.22, 142.47, 145.91, 146.12 (aromatic *ipso*-*C*N and -*Ci*Pr), 160.15 (conjugated *C*=N, enamine-diimine tautomer), 169.01, 171.97 (isolated *C*=N, enamine-diimine tautomer/*C*=N, triimine tautomer) ppm. $C_{43}H_{61}N_3$ (619.98): calcd. C 83.31, H 9.92, N 6.78; found C 82.87, H 9.98, N 6.74. MS (ES$^+$): *m*/*z* = 620.5 [MH]$^+$. IR: $\tilde{\nu}$ = 1631, 1599, 1585 [ν(C=N)], 1537 [ν(C=C), aromatic] cm^{-1}.

1e: 2-*i*PrC$_6$H$_4$NHCMeCHCMeN-2-*i*PrC$_6$H$_4$ (4.45 g, 0.013 mol), *n*BuLi (8.2 mL of a 1.6 M hexane solution, 0.013 mol), MeC(Cl)=N-2-*t*BuC$_6$H$_4$ (3.0 mL, 0.013 mol) and hexane (40 mL) were used. Pale-yellow crystals from methanol/dichloromethane (3.27 g, 50%); m.p. 130–133 °C. ^{1}H NMR (500 MHz, $CDCl_3$), 3 tautomers and 4 geometric isomers possible; (*E*) isomer of 2-*i*PrC$_6$H$_4$NHCMeC[C(Me)=N-2-*i*PrC$_6$H$_4$]CMeN-2-*t*BuC$_6$H$_4$ tautomer dominant (ca. 65%) peaks reported refer to this, unless otherwise stated: δ = 1.04 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$], 1.11 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$] ppm; other isomers: δ = 0.90, 0.94, (2 d, triketimine isomer, ca. 10%), 1.07 [2 overlapping d, (Z) isomer of major tautomer, ca. 25%], 1.28 [s, 9 H, C(CH$_3$)$_3$] ppm; other isomers: δ = 1.13, 1.29, 1.31, 1.38 [4 s, C(CH_3)$_3$], 1.92, 1.96, 2.00 (3 s, 3×3 H, CH_3CN) ppm; other isomers: δ = 1.63, 1.64, 1.74, 1.97, 1.98, 2.09, 2.44 (7 s, CH_3CN), 3.02 [sept, $^3J_{HH}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$] 3.13 [sept, $^3J_{HH}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$] ppm; other isomers: δ = 2.67, 2.88, 2.97, 3.12, 3.26 [5 sept, C*H*(CH$_3$)$_2$], 4.60 (s, α-C*H*, triimine tautomer), 6.53 (dd, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.2 Hz, 1 H, *o*-CH Ar^{iPr} isolated imine), 6.73, (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.2 Hz, 1 H, *o*-CH Ar^{tBu} enamine), 6.82–6.87 (non-first-order m, *o*-CH Ar^{iPr} enamine, 1 H + overlap from other isomers), 6.93–7.12 (non-first-order m, *m*- and *p*-aryl CH, 6 H + overlap from other isomers), 7.18 (dd, 1 H, *m*′-C*H* Ar^{tBu}), 7.24 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz, 1 H, *m*′-C*H* Ar^{iPr}), 7.30 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.3 Hz, 1 H, *m*′-C*H* Ar^{iPr}) ppm; other isomers: δ = 6.45, 6.47, 6.55, 6.60, 6.62, 6.68, 6.83 (dd, *o*-C*H*), 7.15, 7.21, 7.25, 7.29, 7.33 (dd, *m*′-aryl CH) 13.38 (br. s, 1 H, N*H*) ppm; other isomers: δ = 13.20, 13.39, 13.65 (3 br. s) ppm. ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$), peaks due to all isomeric species (unless otherwise specified): δ = 18.42, 19.00 19.35 19.59, 19.76, 20.72, 21.12, 24.61, 25.08, 31.38 (*C*H$_3$CN), 23.06, 23.11, 23.24, 23.28, 23.34, 23.42, 23.59, 29.63, 29.97, 30.36, 30.46 [CH(*C*H$_3$)$_2$ and *t*Bu C(*C*H$_3$)$_3$], 27.42, 27.64, 27.82, 27.88, 28.15 [*C*H(CH$_3$)$_2$], 35.05, 35.18, 35.29 [*t*Bu *C*(CH$_3$)$_3$], 72.46 (α-*C*H, triimine tautomer), 106.41, 111.09 (alkenyl α-*C*, enamine-diimine tautomers), 118.30, 118.57, 119.52, 119.83, 120.61, 123.42, 123.53, 123.89, 123.95, 124.15, 124.19, 124.37, 124.43, 124.55, 124.62, 124.87, 125.18, 125.43, 125.55, 125.71, 125.79, 125.81, 125.86, 125.89, 126.15, 126.21, 126.23, 126.32, 126.50, 126.52, 126.56, 126.63 (aromatic *C*H), 138.06, 138.45, 139.64, 140.17, 141.21, 141.81, 141.87, 142.19, 142.35, 142.51, 142.74, 143.17, 143.83, 144.78, 146.56, 148.44, 148.80, 149.67, 149.94 (aromatic *ipso*-*C*N, -*Ci*Pr and -*Ct*Bu), 156.88, 157.17, 157.50, 158.87, 158.97 (conjugated *C*=N, enamine-diimine tautomers), 167.63, 168.63, 168.72, 169.88, 171.90 (isolated *C*=N, enamine-diimine tautomers/*C*=N, triimine tautomer) ppm. $C_{35}H_{45}N_3$ (507.76): calcd. C 82.79, H 8.93, N 8.28, found C 82.80, H 9.02, N 8.26. MS (ES$^+$): *m*/*z* = 508.4 [MH]$^+$. IR: $\tilde{\nu}$ = 1643, 1608, 1593, 1571 [ν(C=N)] 1537 [ν(C=C), aromatic] cm^{-1}.

1f: 2-*t*BuC$_6$H$_4$NHCMeCHCMeN-2-*t*BuC$_6$H$_4$ (2.0 g, 0.0055 mol), *n*BuLi (3.5 mL of a 1.6 M hexane solution, 0.0055 mol), MeC(Cl)=N-2,6-*i*Pr$_2$C$_6$H$_3$ (1.3 mL, 0.0055 mol) and toluene (40 mL) were used. Pale-yellow powder from methanol (0.60 g, 20%); m.p. 116–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$), peaks due to major (*E*) isomer of 2,6-*i*Pr$_2$C$_6$H$_3$NHCMeC[C(Me)=N-2-*t*BuC$_6$H$_4$] CMeN-2-*t*BuC$_6$H$_4$ (57% abundant; reported integrals normalised): δ = 1.298 [s, 9 H, C(CH_3)$_3$], 1.301 [s, 9 H, C(CH_3)$_3$], 1.00 [d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(*C*H$_3$)$_2$], 1.14 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH-(*C*H$_3$)$_2$], 1.79, 1.94, 2.09 (3 s, 3×3 H, *H*$_3$CCN), 3.06 [2 sept overlapped, $^3J_{HH}$ = 6.7 Hz, 2×1 H, C*H*(CH$_3$)$_2$], 6.47 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz, 1 H, isolated imine aryl *o*-C*H*), 6.68 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz, enamine aryl *o*-C*H*), 6.92–7.10 (non-first-order m, 7 H, aryl *m*- and *p*-CH), 7.29 (d overlapped with minor isomer peaks, 1 H, aryl *m*-C*H*), 7.32 (d, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.2 Hz, 1 H, aryl *m*-C*H*), 13.30 (s), 13.89 (br. s, 1 H, N*H*) ppm; peaks due to (Z) isomer and triketimine form: both 19%, and minor (*E*)-2-*t*BuC$_6$H$_4$NHCMeC[C(Me)=N-2,6-*i*Pr$_2$C$_6$H$_3$]CMeN-2-*t*BuC$_6$H$_4$ isomer, 5%: δ = 0.85, 0.90, 0.94, 1.02, 1.04, 1.06, 1.09, 1.10 [8 d, CH(*C*H$_3$)$_2$], 1.24, 1.28, 1.37, 1.43 [4 s, C(CH_3)$_3$], 1.75, 1.90, 1.93, 1.98, 2.03, 2.08, 2.42 (7 s, *H*$_3$CN), 2.53 [sept, $^3J_{HH}$ = 6.5 Hz, 2 H, triketimine CH(*C*H$_3$)$_2$], 2.88, 2.95 [2 sept, other isomers CH-(*C*H$_3$)$_2$], 4.69 (s, 1 H, α-C*H*, triimine tautomer), 6.42 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2 H, triketimine aryl *o*-C*H*), 6.54 (br. d, *o*-aryl CH), 6.77, 7.26 (2 dd, *m*′-aryl C*H*), 13.25 [s, 1 H, (Z) isomer, N*H*], 13.89 [br. s, minor (*E*) isomer, N*H*]. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), peaks due to all isomeric species (unless otherwise specified): δ = 18.95, 19.03, 19.78, 20.28, 21.54, 21.95, 22.89, 23.00, 23.11, 23.73, 23.85, 23.99, 24.19, 24.41, 24.55, 25.05, 25.44, 30.96, 32.13 [*i*Pr CH(*C*H$_3$)$_2$/*C*H$_3$CN], 27.78, 28.26, 28.47 [*C*H(CH$_3$)$_2$], 29.58, 29.85, 30.44, 30.55, 31.27 [*t*Bu C(*C*H$_3$)$_3$], 35.14, 35.19, 35.29, 36.08 [*t*Bu *C*(CH$_3$)$_3$], 72.84 (α-*C*H, triimine tautomer), 105.97, 111.10 (alkenyl α-*C*, enamine-diimine tautomers), 119.42, 120.51, 121.26, 123.01, 123.21, 123.24, 123.34, 123.57, 123.61, 123.94, 124.16, 124.35, 124.81, 125.15, 125.42, 125.54, 125.70, 125.95, 126.26, 126.31, 126.33, 126.35, 126.45, 126.47, 126.53, 126.59, 126.61 (aromatic *C*H), 136.29, 136.83, 139.20, 139.43, 139.57, 140.23, 142.69, 142.77, 142.98, 143.29, 143.41, 143.48, 143.60, 144.09, 144.34, 144.99, 145.78, 146.93, 149.77, 149.85 (aromatic *ipso*-*C*N, -*Ci*Pr and -*Ct*Bu), 158.07, 158.43, 158.86, 159.61 (conjugated *C*=N, enamine-diimine tautomers), 164.98, 166.16, 167.91, 169.22 (isolated *C*=N, enamine-diimine tautomers/*C*=N, triimine tautomer) ppm. $C_{39}H_{53}N_3$ (563.87): calcd. C 83.07, H 9.47, N 7.45; found C 83.20, H 9.40, N 7.45. MS (ES$^+$): *m*/*z* = 564.4 [MH]$^+$. IR: $\tilde{\nu}$ = 1638, 1602, 1586 [ν(C=N)] 1534 [ν(C=C), aromatic] cm^{-1}.

1g: 2-*i*PrC_6H_4NHCMeCHCMeN-2-*i*PrC_6H_4 (3.55 g, 0.0106 mol), *n*BuLi (6.6 mL of a 1.6 M hexane solution, 0.0106 mol), MeC(Cl)=N-2,6-*i*Pr$_2C_6H_3$ (2.6 mL, 0.0106 mol) and hexane (50 mL) were used. Off-white powder from methanol/dichloromethane (3.39 g, 60%); m.p. 111–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$), peaks due to major isomer (*E*)-2,6-*i*Pr$_2C_6H_3$NHCMeC[C(Me)=N-2-*i*PrC_6H_4]CMeN-2-*i*PrC_6H_4 (65%, reported intensities normalised): δ = 1.03, 1.07, 1.11, 1.14 [4 d, $^3J_{HH}$ = 6.9 Hz, 4 × 6 H, CH(*C*H$_3$)$_2$], 1.79, 1.99, 2.01 (3 s, 3 × 3 H, *H*$_3$CCN), 3.02 [sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.03 [sept, $^3J_{HH}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.14 [sept, $^3J_{HH}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.53 (br. dd, $^3J_{HH}$ = 7.6 Hz, 1 H, isolated imine *o*-aryl C*H*), 6.82 (dd, $^3J_{HH}$ = 7.6 Hz, 1 H, enamine *o*-aryl C*H*), 6.94–7.10 (non-first-order overlapped m, 7 H, *m*- and *p*-aryl C*H*), 7.19 (dd, $^3J_{HH}$ = 7.4 Hz, 1 H, *m*′-aryl C*H*), 7.24 (dd, $^3J_{HH}$ = 7.7 Hz, 1 H, *m*′-aryl C*H*), 13.47 (br. s, 1 H, N*H*) ppm; other isomers {triketimine, 8%, and (*Z*)-2,6-*i*Pr$_2C_6H_3$NHCMeC[C(Me)=N-2-*i*PrC_6H_4]CMeN-2-*i*PrC_6H_4, 27%}: δ = 0.84, 0.90, 0.98, 0.99, 1.01 [5 d, CH(*C*H$_3$)$_2$], 1.49, 1.76, 1.83, 1.95, 2.45(5 s, C*H*$_3$CN), 4.65 (s, 1 H, α-C*H*, triimine tautomer), 2.34, 2.81, 2.90, 2.94, 3.25 [5 sept, CH(*C*H$_3$)$_2$], 6.49, 6.59, 6.66, 7.14, 7.21 (5 dd, aryl C*H*), 13.34 (br. s, N*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), peaks due to all isomeric species (unless otherwise specified): δ = 18.52, 18.53, 18.55, 19.19, 19.22, 20.53, 20.63, 24.60, 24.25, 31.35 (*C*H$_3$CN), 22.64, 22.84, 22.94, 22.99, 23.02, 23.13, 23.15, 23.24, 23.31, 23.54, 23.67, 23.72, 24.18, 24.28 [CH(*C*H$_3$)$_2$], 27.45, 27.83, 27.88, 28.08, 28.36, 28.56 [*C*H(CH$_3$)$_2$], 72.32 (α-*C*H, triimine tautomer), 104.64, 109.66 (alkenyl α-*C*, enamine-diimine tautomers), 118.31, 118.46, 119.81, 122.94, 123.02, 123.13, 123.16, 123.36, 123.54, 123.83, 123.86, 123.94, 124.22, 124.54, 124.59, 124.60, 124.90, 125.22, 125.48, 125.53, 125.68, 125.71, 125.74, 125.79, 125.93, 125.99, 126.14, 126.23 (aromatic *C*H), 136.36, 138.04, 138.35, 139.37, 140.50, 141.27, 141.64, 141.95, 142.12, 142.34, 142.37, 142.55, 143.09, 146.65, 148.53, 148.84 (aromatic *ipso*-*C*N and -*Ci*Pr), 157.64, 157.80, 158.64, 158.86, 159.80 (conjugated *C*=N, enamine-diimine tautomers), 168.62, 170.10, 171.84 (isolated *C*=N, enamine-diimine tautomers/*C*=N, triimine tautomer) ppm. $C_{37}H_{49}N_3$ (535.81): calcd. C 82.94, H 9.22, N 7.84; found C 82.69, H 9.27, N 7.78. MS (ES$^+$): *m*/*z* = 536.4 [MH]$^+$. IR: $\tilde{\nu}$ = 1593 (br.) [ν(C=N)] 1537 [ν(C=C), aromatic] cm^{-1}.

1h: 2-*i*PrC_6H_4NHCMeCHCMeN-2-*i*PrC_6H_4 (10.11 g, 0.0302 mol), *n*BuLi (19.5 mL of a 1.6 M hexane solution, 0.0312 mol), *t*BuC(Cl)=N-2,4,6-Me$_3C_6H_2$ (7.20 mL, 0.0303 mol) and hexane (70 mL) were used. Colourless crystals from methanol/dichloromethane (11.36g, 71%); m.p. 144–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99, 1.01 [2 overlapping d, $^3J_{HH}$ = 7.0 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.17 [br. s, 9 H, C(C*H*$_3$)$_3$], 1.88 (br. s, 6 H, C*H*$_3$CN), 2.02 (s, 6 H, Mes *o*-C*H*$_3$), 2.16 (s, 3 H, Mes *p*-C*H*$_3$), 3.02 [sept, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*(CH$_3$)$_2$], 4.83 (br. s, 1 H, α-CH), 6.47 (dd, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz, 2 H, *o*-aryl C*H*), 6.69 (br. s, 2 H, Mes C*H*), 6.96, 7.02 (td, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3 Hz, 2 × 2 H, *p*- and *m*-aryl C*H*), 7.18 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.3 Hz, 2 H, *m*′-aryl C*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.32 (Mes *o*-*C*H$_3$), 20.62 (Mes *p*-*C*H$_3$), 21.01 (*C*H$_3$CN), 23.20, 23.31 [CH(*C*H$_3$)$_2$], 27.51 [*C*H(CH$_3$)$_2$], 28.91 [C(*C*H$_3$)$_3$], 43.49 [*C*(CH$_3$)$_3$], 67.86 (α-*C*H), 118.21 [Ar^{iPr} (–N=C) *o*-*C*H], 123.56 [Ar^{iPr} (–N=C) *p*-*C*H], 125.61 (Ar^{iPr} *m*′-*C*H), 126.03 (Ar^{iPr} *m*-*C*H), 128.37 (Mes *C*H), 130.71 (br., Mes *ipso*-*C*CH$_3$), 138.17 (Ar^{iPr} *ipso*-*Ci*Pr), 146.46, 148.65 (aromatic *ipso*-*C*N), 169.58 (*C*=N) ppm. $C_{37}H_{49}N_3$ (535.81): calcd. C 82.94, H 9.22, N 7.84; found C 83.46, H 9.61, N 7.81. MS (ES$^+$): *m*/*z* = 536.5 [MH]$^+$. IR: $\tilde{\nu}$ = 1683, 1659 [ν(C=N)] 1595, 1571 [ν(C=C), aromatic] cm^{-1}.

1i: 2,6-*i*Pr$_2C_6H_3$NHCMeCHCMeN-2,6-*i*Pr$_2C_6H_3$ (3.68 g, 0.0088 mol), *n*BuLi (5.5 mL of a 1.6 M hexane solution, 0.0088 mol), MeC(Cl)=N-2-*i*PrC_6H_4 (1.8 mL, 0.0088 mol) and hexane (40 mL) were used. Large yellow crystals from methanol/dichloromethane (2.82 g, 56%); m.p. 139–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$), peaks from triketimine form (9%) + (*E*)- and (*Z*)-2,6-*i*Pr$_2C_6H_3$NHCMeC[C(Me)=N-2-*i*PrC_6H_4]CMeN-2,6-*i*Pr$_2C_6H_3$ (*E*)/(*Z*) = 45%:39%) + (*E*)-2,6-*i*Pr$_2C_6H_3$NHCMeC[C(Me)=N-2,6-*i*Pr$_2C_6H_4$]CMeN-2-*i*Pr$_2C_6H_4$ (7%): δ = 0.89, 0.94, 1.02–1.15 (multiple overlapping d, 30 H, CH(C*H*$_3$)$_2$], 1.56, 1.57, 1.81, 1.83, 1.85, 1.94, 1.99, 2.05, 2.43 (9 s, 9 H, CH$_3$CN), 2.55, 2.86–3.19, 3.26 (multiple overlapping sept, 5 H, C*H*(CH$_3$)$_2$], 6.47, 6.51, 6.64, 6.82 (4 dd, 1 H, *o*-aryl CH), 6.97–7.09, 7.15–7.24 (2 non-first-order m, 9 H, *m*-, *m*′- and *p*-aryl C*H*), 4.71, 13.08, 13.10, 13.83 (4 s, 1 H, α-C*H*, triimine tautomer + N*H*, enamine-diimine tautomers) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$), peaks due to all isomeric species (unless otherwise specified): δ = 18.45, 18.96, 20.89, 24.38, 24.68, 31.49 [*C*H$_3$C(N)], 22.93, 23.08, 23.10, 23.18, 23.20, 23.35, 23.37, 23.41, 23.50, 23.71, 23.81, 23.86, 23.99, 24.15, 24.32 [CH(*C*H$_3$)$_2$], 27.46, 27.85, 27.90, 28.31 28.37, 28.40 [*C*H(CH$_3$)$_2$], 103.88, 108.55 (alkenyl α-*C*, enamine-diimine tautomers), 118.31, 119.73, 122.96, 123.00, 123.14, 123.18, 123.23, 123.27, 123.37, 123.61, 123.91, 124.62, 124.72, 124.76, 125.34, 125.36, 125.61, 125.76, 125.25 (aromatic *C*H), 136.36, 136.49, 136.85, 138.24, 139.89, 140.19, 141.40, 142.14, 142.23, 142.52, 146.01, 146.62, 148.61, 148.96 (aromatic *ipso*-*C*N and -*Ci*Pr), 158.83, 159.44 (conjugated *C*=N, enamine-diimine tautomers), 169.05, 169.46, 169.65, 170.04, 171.72 (isolated *C*=N, enamine-diimine tautomers/*C*=N, triimine tautomer) ppm. $C_{40}H_{55}N_3$ (577.89): calcd. C 83.14, H 9.59, N 7.27, found C 83.36, H 9.69, N 7.26. MS (ES$^+$): *m*/*z* = 578.3 [MH]$^+$. IR: $\tilde{\nu}$ = 1617, 1589, 1602 [ν(C=N)] 1537 [ν(C=C), aromatic] cm^{-1}.

1j: 2-*i*PrC_6H_4NHCMeCHCMeN-2-*i*PrC_6H_4 (14.0 g, 0.0419 mol), *n*BuLi (26.2 mL of a 1.6 M hexane solution, 0.0419 mol), *t*BuC(Cl)=N-2-MeOC_6H_4 (9.5 mL, 0.0419 mol) and hexane (100 mL) were used. Large pale-yellow blocks from methanol (10.15 g, 46%), m.p. 107–109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) peaks for single isomer (*Z*)-2-*i*PrC_6H_4NHCMeC[C(*t*Bu)=N-2-MeO-C_6H_4]CMeN-2-*i*PrC_6H_4: δ = 0.91 (d, $^3J_{HH}$ = 6.8 Hz, 6 H), 0.94 [d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.33 [s, 9 H, C(C*H*$_3$)$_3$] 1.68 (s, 6 H, C*H*$_3$CN), 2.71 [sept, $^3J_{HH}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.61 (s, 3 H, OC*H*$_3$), 6.46 (dd, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.3 Hz, 1 H, Ar^{OMe} *o*-C*H*), 6.61 (dd, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 1.1 Hz, 2 H, Ar^{iPr} *o*-C*H*), 6.70 (br. dd, $^3J_{HH}$ = 8.0 Hz, 1 H, Ar^{OMe} *m*′-C*H*), 6.74 (td, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.0 Hz, 1 H, Ar^{OMe} *p*-C*H*), 6.90 (td, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.6 Hz, 1 H, Ar^{OMe} *m*-C*H*), 6.95, 6.98 (2 non-first-order td, 4 H, Ar^{iPr} *m*- and *p*-C*H*), 7.10 (dd, $^3J_{HH}$ = 6.9, $^4J_{HH}$ = 2.4 Hz, 2 H, Ar^{iPr} *m*′-*C*H), 13.48 (br. s, 1 H, N*H*) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 20.65 (*C*H$_3$CN), 23.16 [CH(*C*H$_3$)$_2$], 27.93 [*C*H(CH$_3$)$_2$], 30.73 [C(*C*H$_3$)$_3$], 42.16 [*C*(CH$_3$)$_3$], 55.21 (O*C*H$_3$), 104.53 (alkenyl α-*C*), 111.12 (Ar^{OMe} *m*′-*C*H), 119.32 (Ar^{OMe} *o*-*C*H), 120.17 (Ar^{OMe} *p*-*C*H), 124.04 (Ar^{OMe} *m*-*C*H), 124.41 (Ar^{iPr} *o*-*C*H), 125.65 (Ar^{iPr} *p*-*C*H), 125.69 (Ar^{iPr} *m*′-*C*H), 125.90 (Ar^{iPr} *m*-*C*H), 140.85 (Ar^{iPr} *ipso*-*Ci*Pr), 141.83, 142.84 (aromatic *ipso*-*C*N), 150.34 (Ar^{OMe} *ipso*-*C*OCH$_3$), 158.61 (conjugated *C*=N), 182.36 (isolated *C*=N) ppm. $C_{35}H_{45}N_3O$ (523.76): calcd. C 80.26, H 8.66, N 8.02, found C 80.79, H 8.57, N 8.08. MS (ES$^+$): *m*/*z* = 524.4 [MH]$^+$. IR: $\tilde{\nu}$ = 1604, 1589 [ν(C=N)] 1531 [ν(C=C), aromatic] cm^{-1}.

1k: 2-*i*PrC_6H_4NHCMeCHCMeN-2-*i*PrC_6H_4 (3.34 g, 0.0100 mol), *n*BuLi (6.3 mL of a 1.6 M hexane solution, 0.0101 mol), PhC(Cl)=N-2-*i*PrC_6H_4 (2.70 mL, 0.0105 mol) and diethyl ether (20 mL) were used. Large yellow crystals from methanol/dichloromethane (3.63 g, 65%), m.p. 121–124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) peaks for single isomer (*Z*)-2-

*i*PrC$_6$H$_4$NHCMeC[C(Ph)=N-2-*i*PrC$_6$H$_4$]CMeN-2-*i*PrC$_6$H$_4$: δ = 0.98, 1.01, 1.16 [3 d, $^3J_{HH}$ = 6.9 Hz, 3×6 H, CH(CH_3)$_2$], 1.56 (s, 6 H, CH_3CN), 2.82 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H), 3.31 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H) [2 C*H*(CH$_3$)$_2$], 6.66–6.70 (non-first-order m, 2 H, enamine aryl *o*-C*H*), 6.73–6.77 (non-first-order m, 1 H, isolated imine aryl *o*-C*H*), 6.97–7.02 (non-first-order m, 4 H, enamine aryl *m*- and *p*-C*H*), 7.03–7.07 (non-first-order m, 2 H, isolated imine aryl *m*- and *p*-C*H*) 7.12–7.14 (non-first-order m, 2 H, enamine aryl *m*′-C*H*), 7.20–7.24 (non-first-order m, 1 H, isolated imine aryl *m*′-C*H*), 7.37–7.43 (non-first-order m, 3 H, *m*- and *p*-Ph), 8.09–8.13 (dd, $^3J_{HH}$ = 7.6 Hz, 2 H, *o*-Ph), 13.56 (br. s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 18.19 (*C*H$_3$CN), 22.05, 22.11, 22.20 [CH(*C*H$_3$)$_2$], 26.99 [*C*H(CH$_3$)$_2$], 101.15 (alkenyl α-*C*), 118.05, 123.27, 123.73, 123.88, 124.08, 124.49, 124.69, 124.86, 127.37, 127.52, 129.25 (aromatic *C*H), 140.64, 140.80, 141.40, 141.47,146.00 (aromatic *ipso*-*C*N and -*Ci*Pr), 158.44 (conjugated *C*=N), 165.34 (isolated *C*=N) ppm. C$_{39}$H$_{45}$N$_3$ (555.80): calcd. C 84.28, H 8.16, N 7.56; found C 84.08, H 8.05, N 7.53. MS (ES$^+$): *m*/*z* = 556.4 [MH]$^+$. IR: $\tilde{\nu}$ = 1607, 1589, 1569 [ν(C=N)] 1543 [ν(C=C), aromatic] cm^{-1}.

Carbonylmetal Complexes: None of the compounds described below showed a clear melting point. However, all of the chromium complexes darken slowly above ca. 250 °C, and all of the molybdenum and tungsten complexes darken slowly above ca. 300 °C. A typical procedure is given in full for **2a**. All other carbonylmetal complexes were prepared analogously. Outline data, and deviations from standard procedure, are given for other cases. **1d** gave no reaction with Cr(CO)$_6$ or Mo(CO)$_6$ under similar conditions to those described for other examples. **1f** gave some product, but solutions decomposed during attempts at characterization. **1i** gave some product which decomposed over 1–2 d even in the solid state. Examples listed are indefinitely stable in the solid state in air, and are stable for a number of hours in solution if protected from light.

1a·Cr(CO)$_3$ (2a): A magnetically stirred mixture of **1a** (0.493 g, 0.001 mol) and hexacarbonylchromium (0.220 g, 0.001 mol) in di-*n*-butyl ether (20 mL) and thf (1 mL) were heated to reflux. A red precipitate became visible after approximately 20 min; heating was continued for a further 4 h. After cooling, the mixture was stirred at room temperature overnight, then the red precipitate (**2a**) was collected by filtration, washed with hexane (4×10 mL), and dried. Yield: 0.48 g, 82%. ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.07 [d, $^3J_{HH}$ = 6.8 Hz, 9 H, CH(CH_3)$_2$], 1.43 [d, $^3J_{HH}$ = 6.8 Hz, 9 H, CH(CH_3)$_2$], 2.29 (s, 9 H, CH_3C=N), 2.80 [sept, $^3J_{HH}$ = 6.8 Hz, 3 H, C*H*(CH$_3$)$_2$], 5.65 (s, 1 H, α-C*H*), 6.72 (d, $^3J_{HH}$ = 7.5 Hz, 3 H, *o*-C*H*), 7.21, 7.25 (2 overlapping t, $^3J_{HH}$ = 7.2 Hz, 2×3 H, *m*- and *p*-C*H*), 7.41 (d, $^3J_{HH}$ = 7.3 Hz, 3 H, *m*′-C*H*) ppm. ^{13}C{^{1}H}NMR (100.65 MHz, [D$_6$]dmso): δ = 22.85 (*C*H$_3$CHCH$_3$), 24.22 (CH$_3$CH*C*H$_3$), 25.67 (*C*H$_3$C=N), 26.99 (CH$_3$*C*HCH$_3$), 64.42 (α-*C*H), 120.69, 125.75, 125.81, 126.21 (4 aryl *C*H), 137.35 [aryl *C*-CH(CH$_3$)$_2$], 149.84 (aryl *C*–N), 175.21 (N=*C*), 232.14 (Cr–*C*O) ppm. C$_{37}$H$_{43}$CrN$_3$O$_3$ (629.76): calcd. C 70.57, H 6.88, N 6.67, found C 69.73, H 6.93, N 6.53. IR: $\tilde{\nu}$ = 1893, 1796, 1775 [ν(C=O)] δ = 1619, 1598, 1574 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 330 (π^*←*n*, br., tailing into π^*←π), 469, 550 [shoulder (MLCT)] nm.

1a·Mo(CO)$_3$ (3a): Ligand **1a** (0.990 g, 0.002 mol), hexacarbonylmolybdenum (0.53 g, 0.002 mol), *n*Bu$_2$O (40 mL) and thf (2 mL) were heated to reflux for 1 h and 45 min. Orange powder (0.80 g, 60%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.10 [d, $^3J_{HH}$ = 6.7 Hz, 9 H, CH(CH_3)$_2$] 1.41 [d, $^3J_{HH}$ = 6.7 Hz, 9 H, CH(CH_3)$_2$], 2.31 (s, 9 H, CH_3C=N), 2.91 [sept, $^3J_{HH}$ = 6.7 Hz, 3 H, C*H*(CH$_3$)$_2$], 5.66 (br. s, 1 H, α-C*H*), 6.69 (d, $^3J_{HH}$ = 7.5 Hz, 3 H, *o*-C*H*), 7.22, 7.27 (2 overlapping t, $^3J_{HH}$ = 7.3 Hz, 2×3 H, *m*- and *p*-C*H*), 7.41 (d, $^3J_{HH}$ = 7.5 Hz, 3 H, *m*′-C*H*) ppm. ^{13}C{^{1}H}NMR (100.65 MHz, [D$_6$]dmso): δ = 22.76 (*C*H$_3$CHCH$_3$), 24.07 (CH$_3$CH*C*H$_3$), 25.42 (*C*H$_3$C=N), 27.11 (CH$_3$*C*HCH$_3$), 65.23 (α-*C*H), 120.33, 125.86, 126.01, 126.26 (4 aryl *C*H), 137.47 [aryl *C*–CH(CH$_3$)$_2$], 149.22 (aryl *C*–N), 175.99 (N=*C*), 218.39 (Mo–*C*O) ppm. C$_{37}$H$_{43}$MoN$_3$O$_3$ (673.71): calcd. C 65.96, H 6.43, N 6.24; found C 66.05, H 6.50, N 6.24. IR: $\tilde{\nu}$ = 1897, 1787, 1776 [ν(C=O)] 1618, 1599, 1574 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 290 (π^*←n, tailing into π^*←π), 444, 510 [shoulder (MLCT)] nm.

1a·W(CO)$_3$ (4a): Ligand **1a** (0.250 g, 0.0005 mol), W(CO)$_6$ (0.180 g, 0.0005 mol), *n*Bu$_2$O (10 mL), thf (1.2 mL) and trimethylamine *N*-oxide (0.170 g, 0.0015 mol) were stirred for 30 min, then heated to 100 °C for 2 h, then stirred overnight. Dark-crimson precipitate (0.11g, 29%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.10 [d, $^3J_{HH}$ = 6.7 Hz, 9 H, CH(CH_3)$_2$] 1.39 [d, $^3J_{HH}$ = 6.7 Hz, 9 H, CH(CH_3)$_2$], 2.31 (s, 9 H, CH_3C=N), 2.82 [sept, $^3J_{HH}$ = 6.7 Hz, 3 H, C*H*(CH$_3$)$_2$], 5.62 (br. s, 1 H, α-C*H*), 6.69 (d, $^3J_{HH}$ = 7.2 Hz, 3 H, *o*-C*H*), 7.22, 7.25 (2 overlapping t, $^3J_{HH}$ = 7.2 Hz, 2×3 H, *m*- and *p*-C*H*), 7.39 (d, $^3J_{HH}$ = 7.2 Hz, 3 H, *m*′-C*H*) ppm. ^{13}C{^{1}H}NMR (100.65 MHz, [D$_6$]dmso): δ = 22.32 (*C*H$_3$CHCH$_3$), 24.06 (CH$_3$CH*C*H$_3$), 25.52 (*C*H$_3$C=N), 27.08 (CH$_3$*C*HCH$_3$), 67.26 (α-*C*H), 120.89, 125.86, 126.16, 126.26 (4 aryl *C*H), 137.41 [aryl *C*–CH(CH$_3$)$_2$], 149.22 (aryl *C*–N), 175.99 (N=*C*), 206.48 (W–*C*O) ppm. IR: $\tilde{\nu}$ = 1889, 1785, 1775 [ν(CO)] 1620, 1599, 1575 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 325 (π^*←n, tailing into π^*←π), 450, 530 [br. shoulder (MLCT)] nm.

1b·Cr(CO)$_3$ (2b): Ligand **1b** (0.570 g, 0.000988 mol), Cr(CO)$_6$ (0.222 g, 0.00101 mol), *n*Bu$_2$O (15 mL) and thf (1 mL) were heated to reflux for 6.5 h. Red powder (0.478 g, 68%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.09, 1.16, 1.20, 1.28 [4 d, $^3J_{HH}$ = 6.7 Hz, 4×3 H, CH(CH_3)$_2$], 1.38–1.41 [2 overlapping d, 2×3 H, CH-(CH_3)$_2$], 1.44, 1.54 [2 d, 2×3 H, CH(CH_3)$_2$], 1.12 [s, 9 H, C-(CH_3)$_3$], 2.25, 2.28 (2 s, 2×3 H, CH_3C=N), 2.63, 2.72, 2.93, 3.33 [4 sept, $^3J_{HH}$ = 6.7 Hz, 4×1 H, C*H*(CH$_3$)$_2$], 6.06 (s, 1 H, α-C*H*), 6.84–6.87 (non-first-order m, 1 H), 7.09–7.11 (non-first-order m, 1 H), 7.16–7.30 (non-first-order m, 7 H), 7.44–7.48 (non-first-order m, 2 H, aromatic C*H*) ppm. C$_{43}$H$_{55}$CrN$_3$O$_3$ (713.92): calcd. C 72.34, H 7.76, Cr 7.28, N 5.89; found C 72.31, H 8.02, Cr 7.18, N 5.81. IR: $\tilde{\nu}$ = 1894, 1796, 1770 [ν(C=O)] 1617, 1599, 1572 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 289, 345 [shoulder (π^*←n, π^*←π)], 475, 550 [shoulder (MLCT)] nm.

1b·Mo(CO)$_3$ (3b): Ligand **1b** (0.571 g, 0.000990 mol), Mo(CO)$_6$ (0.260 g, 0.000985 mol), *n*Bu$_2$O (15 mL) and thf (3 mL) were heated to reflux for 6 h. Red powder (0.640 g, 86%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.08–1.50 [multiple d, 24 H, CH-(CH_3)$_2$], 1.15 [s, 9 H, C(CH_3)$_3$], 2.27, 2.30 (2 s, 2×3 H, CH_3C=N), 2.82, 3.00, 3.09, 3.29 [4 sept, $^3J_{HH}$ = 6.7 Hz, 4×1 H, C*H*(CH$_3$)$_2$], 6.05 (s, 1 H, α-C*H*), 6.74–6.78 (non-first-order m, 1 H), 6.95 (br. d, 1 H), 7.15–7.21 (non-first-order m, 3 H), 7.23–7.31 (non-first-order m, 4 H), 7.44–7.48 (non-first-order m, 2 H, aromatic C*H*) ppm. C$_{43}$H$_{55}$MoN$_3$O$_3$ (757.87): calcd. C 68.15, H 7.31, Mo 12.66, N 5.54; found C 67.49, H 7.42, Mo 11.84, N 5.40. IR: $\tilde{\nu}$ = 1900, 1799, 1769 [ν(C=O)] 1617, 1597, 1572 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 290, 345 [weak br. shoulder (π^*←n, π^*←π)], 447, 515 [shoulder (MLCT)] nm.

1c·Cr(CO)$_3$ (2c): Ligand **1c** (0.538 g, 0.00101 mol), Cr(CO)$_6$ (0.217 g, 0.000986 mol), *n*Bu$_2$O (15 mL) and thf (1 mL) were heated to reflux for 5 h. Bright-red powder (0.310 g, 47%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.06, 1.10, 1.24, 1.43, 1.47, 1.51 [6 d, $^3J_{HH}$ = 6.8 Hz, 6×3 H, CH(CH_3)$_2$], 1.14 [s, 9 H, C(CH_3)$_3$], 2.25, 2.27 (2 s, 2×3 H, CH_3C=N), 2.73–2.83 [3 overlapping sept,

$^3J_{HH}$ = 6.8 Hz, 3×1 H, C*H*(CH$_3$)$_2$], 6.06 (s, 1 H, α-C*H*), 6.75 (dd, $^3J_{HH}$ = 7.6 Hz, 1 H), 6.79 (dd, $^3J_{HH}$ = 7.5 Hz, 1 H), 6.82 (dd, $^3J_{HH}$ = 7.6 Hz, 1 H), 7.07–7.13 (non-first-order m, 2 H), 7.20–7.26 (non-first-order m, 5 H), 7.42 (2 overlapping d, 2×1 H, aromatic C*H*) ppm. $C_{40}H_{49}CrN_3O_3$ (671.84): calcd. C 71.51, H 7.35, Cr 7.74, N 6.25; found C 69.79, H 7.08, Cr 7.64, N 5.95. IR: $\tilde{\nu}$ = 1898, 1802, 1770 [ν(C=O)] 1620, 1597, 1578 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 290, 330 [shoulder (π*←n, π*←π)], 471, 550 [shoulder (MLCT)] nm.

1c·Mo(CO)$_3$ (3c): Ligand **1c** (0.540 g, 0.00101 mol), Mo(CO)$_6$ (0.268 g, 0.00102 mol), *n*Bu$_2$O (15 mL) and thf (1 mL) were heated to reflux for 6 h. Red powder (0.448 g, 63%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.07, 1.12, 1.26, 1.40, 1.44, 1.47 [6 d, $^3J_{HH}$ = 6.8 Hz, 6×3 H, CH(C*H*$_3$)$_2$], 1.17 [s, 9 H, C(C*H*$_3$)$_3$], 2.27, 2.28 (2 s, 2×3 H, C*H*$_3$C=N), 2.83 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H), 2.91 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.04 (s, 1 H, α-C*H*), 6.72, 6.74 (2 overlapping d, 2×1 H), 6.81 (dd, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 2 Hz, 1 H), 7.07–7.13 (non-first-order m, 2 H), 7.20–7.29 (non-first-order m, 5 H), 7.41, 7.43 (2 overlapping d, 2×1 H, aromatic C*H*) ppm. $C_{40}H_{49}MoN_3O_3$ (715.79): calcd. C 67.12, H 6.90, Mo 13.40, N 5.87; found C 65.40, H 6.84, Mo 13.11, N 5.63. IR: $\tilde{\nu}$ = 1904, 1803, 1769 [ν(C=O)] 1617, 1597, 1586, 1576 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 289, 340 [weak br. shoulder (π*←n, tailing into π*←π)], 445, 505 [shoulder (MLCT)] nm.

1e·Cr(CO)$_3$ (2e): Ligand **1e** (0.507 g, 0.001 mol), Cr(CO)$_6$ (0.220 g, 0.001 mol), *n*Bu$_2$O (20 mL) and thf (1 mL) were heated to reflux for 5 h. Bright-red powder (0.580 g, 90%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.08 [d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.12 [d, $^3J_{HH}$ = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.43, 1.44 [2 overlapping d, $^3J_{HH}$ = 6.7 Hz, 2×3 H, CH(C*H*$_3$)$_2$], 1.38 [s, 9 H, C(C*H*$_3$)$_3$], 2.24 (s, 3 H), 2.29 (s, 6 H, C*H*$_3$C=N), 2.67 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H), 2.70 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 5.63 (br. s, 1 H, α-C*H*), 6.75, 6.84 (2 non-first-order m, 2×1 H), 7.09 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, *o*-C*H*), 7.14–7.27 (non-first-order m, 6 H, *m*- and *p*-C*H*), 7.40–7.45 (non-first-order m, 2 H), 7.52–7.56 (non-first-order m, 1 H, *m*′-CH) ppm. $C_{38}H_{45}CrN_3O_3$ (643.79): calcd. C 70.90, H 7.05, Cr 8.08, N 6.53; found C 70.90, H 7.27, Cr 8.04, N 6.42. IR: $\tilde{\nu}$ = 1894, 1796, 1772 [ν(C=O)] 1617, 1598, 1573 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 330 (br., π*←n, tailing into π*←π), 471, 540 [shoulder (MLCT)] nm.

1e·Mo(CO)$_3$ (3e): Ligand **1e** (0.260 g, 0.000513 mol), Mo(CO)$_6$ (0.133 g, 0.000504 mol), *n*Bu$_2$O (15 mL) and thf (1 mL) were heated to reflux for 7 h. Orange powder (0.240 g, 69%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 0.98, 1.01 [2 d, $^3J_{HH}$ = 6.5 Hz, 2×3 H, CH(C*H*$_3$)$_2$], 1.29, 1.33 [2 overlapped d, 6 H, CH(C*H*$_3$)$_2$], 1.29 [s, 9 H, *t*Bu C(C*H*$_3$)$_3$], 2.16 (s, 3 H, C*H*$_3$C=N), 2.19 [s, 6 H, (C*H*$_3$C=N)], 2.73 (sept, $^3J_{HH}$ = 6.5 Hz, 1 H), 2.74 (sept, $^3J_{HH}$ = 6.5 Hz, 1 H, C*H*(CH$_3$)$_2$], 5.54 (s, 1 H, α-C*H*), 6.60 (d, $^3J_{HH}$ = 6.8 Hz, 1 H), 6.67 (d, $^3J_{HH}$ = 7.1 Hz, 1 H), 6.86 (d, $^3J_{HH}$ = 7.5 Hz, 1 H) (3 *o*-C*H*), 7.03–7.21 (non-first-order m, 6 H, *m*- and *p*-C*H*), 7.31, 7.32 (2 overlapping d, 2×1 H), 7.43 (d, $^3J_{HH}$ = 6.9 Hz, 1 H, *m*′-C*H*) ppm. $C_{38}H_{45}MoN_3O_3$ (687.73): calcd. C 66.37, H 6.59, Mo 13.96, N 6.11; found C 64.34, H 6.60, Mo 13.34, N 5.79. IR: $\tilde{\nu}$ = 1898, 1792, 1773 [ν(C=O)] 1617, 1597, 1578, 1571 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 290 (π*←n, tailing into π*←π), 444, 510 [shoulder (MLCT)] nm.

1g·Cr(CO)$_3$ (2g): Ligand **1g** (0.500 g, 0.000930 mol), Cr(CO)$_6$ (0.20 g, 0.000930 mol), *n*Bu$_2$O (30 mL) and thf (1 mL) were heated to reflux for 5 h. Dark-red powder (0.38 g, 60%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 0.99, 1.13 [2 overlapping d, 2×6 H, CH(C*H*$_3$)$_2$], 1.27–1.58 [non-first-order m, 12 H, CH(C*H*$_3$)$_2$], 2.26, 2.29 (2 overlapping s, 3 + 6 H, C*H*$_3$C=N), 2.87–3.16 [multiple poorly defined sept, 4 H, C*H*(CH$_3$)$_2$], 5.64 (br. s, 1 H, α-C*H*), 6.71–7.51 (poorly defined m, 11 H, aromatic C*H*) ppm. $C_{40}H_{49}CrN_3O_3$ (671.84): calcd. C 71.51, H 7.35, Cr 7.74, N 6.25; found C 70.76, H 7.49, Cr 7.87, N 6.08. IR: $\tilde{\nu}$ = 1893, 1792, 1770 [ν(C=O)] 1612, 1599, 1578 [ν(C=N)] cm^{-1}. λ_{max} = 340 (π*←n, broad, tailing into π*←π), 471, 550 [shoulder (MLCT)] nm.

1g·Mo(CO)$_3$ (3g): Ligand **1g** (0.500 g, 0.000930 mol), Mo(CO)$_6$ (0.247 g, 0.000930 mol), *n*Bu$_2$O (30 mL) and thf (1 mL) were heated to reflux for 3.5 h. Bright-red powder (0.62 g, 93%). ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 0.93–1.49 [multiple d, 24 H, CH(C*H*$_3$)$_2$], 2.28–2.36 (multiple s, 9 H, C*H*$_3$C=N), 2.80–3.17 [multiple sept, 4 H, C*H*(CH$_3$)$_2$], 5.66 (br. s, 1 H, α-C*H*), 6.50–7.48 (non-first-order m, 11 H, aromatic C*H*) ppm. $C_{40}H_{49}MoN_3O_3$ (715.79): calcd. C 67.12, H 6.90, Mo 13.40, N 5.87; found C 65.70, H 7.21, Mo 12.08, N 5.70. IR: $\tilde{\nu}$ = 1897, 1790, 1774 [ν(C=O)] 1612, 1597, 1578, 1571 [ν(C=N)] cm^{-1}.

1h·Cr(CO)$_3$ (2h): Ligand **1h** (0.533 g, 0.000997 mol), Cr(CO)$_6$ (0.218 g, 0.00991 mol), *n*Bu$_2$O (15 mL) and thf (1 mL) were heated to reflux for 7 h. Deep-red powder (0.520 g, 78%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.08–1.09 [m, 6 H, CH(C*H*$_3$)$_2$], 1.27, 1.42 [2 d, $^3J_{HH}$ = 6.7 Hz, 2×3 H, CH(C*H*$_3$)$_2$], 1.11 [s, 9 H, C(C*H*$_3$)$_3$], 2.13, 2.22, 2.24, 2.25, 2.28 (5 s, 5×3 H, C*H*$_3$C=N and Mes C*H*$_3$), 2.67, 2.83 (2 sept, $^3J_{HH}$ = 6.7 Hz, 2×1 H, C*H*(CH$_3$)$_2$], 6.06 (s, 1 H, α-C*H*), 6.78 (s, 1 H), 6.81 (s, 1 H, aromatic Mes C*H*), 6.87–6.91 (non-first-order m, 1 H), 7.07–7.11 (non-first-order m, 1 H), 7.20–7.28 (non-first-order m, 4 H), 7.40–7.46 (non-first-order m, 2 H, aromatic C*H*) ppm. $C_{40}H_{49}CrN_3O_3$ (671.84): calcd. C 71.51, H 7.35, Cr 7.74, N 6.25; found C 71.50, H 7.69, Cr 7.62, N 6.19. IR: $\tilde{\nu}$ = 1894, 1796, 1773 [ν(C=O)] 1612, 1598, 1578 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 289, 355 [shoulder (π*←n, π*←π)], 470, 550 [shoulder (MLCT)] nm.

1h·Mo(CO)$_3$ (3h): Ligand **1h** (0.535 g, 0.001 mol), Mo(CO)$_6$ (0.266 g, 0.00101 mol), *n*Bu$_2$O (15 mL) and thf (3 mL) were heated to reflux for 7 h. Bright-red powder (0.588 g, 82%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.08, 1.10, 1.25, 1.41 [4 d, $^3J_{HH}$ = 6.8 Hz, 4×3 H, CH(C*H*$_3$)$_2$], 1.13 [s, 9 H, C(C*H*$_3$)$_3$], 2.18 (s, 3 H), 2.23 (s, 3 H), 2.25 (s, 6 H), 2.29 (s, 3 H, C*H*$_3$C=N and Mes C*H*$_3$), 2.87, 2.88 [2 sept, $^3J_{HH}$ = 6.8 Hz, 2×1 H, C*H*(CH$_3$)$_2$], 6.05 (s, 1 H, α-C*H*), 6.78, 6.80 (s, 2×1 H, Mes *m*- + *m*′-C*H*), 6.81–6.85 (non-first-order m, 1 H), 6.96 (d, $^3J_{HH}$ = 7.5 Hz, 1 H), 7.20–7.29 (non-first-order m, 4 H), 7.40–7.46 (non-first-order m, 2 H, aromatic C*H*) ppm. $C_{40}H_{49}MoN_3O_3$ (715.79): calcd. C 67.12, H 6.90, Mo 13.40, N 5.87; found C 66.43, H 6.97, Mo 12.60, N 5.75. IR: $\tilde{\nu}$ = 1899, 1799, 1772 [ν(C=O)] 1612, 1598, 1576 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 290, 345 [weak br. shoulder (π*←n, π*←π)], 445, 508 [shoulder (MLCT)] nm.

1j·Cr(CO)$_3$ (2j): Ligand **1j** (0.525 g, 0.001 mol), Cr(CO)$_6$ (0.221 g, 0.001 mol), *n*Bu$_2$O (20 mL) and thf (1 mL) were heated to reflux for 5.5 h. Red powder (0.481 g, 73%). ^{1}H NMR (500 MHz, [D$_6$]-dmso): δ = 1.05, 1.08, 1.41, 1.45 [4 poorly defined d, 4×3 H, CH(C*H*$_3$)$_2$], 1.12 [s, 9 H, C(C*H*$_3$)$_3$], 2.21, 2.23 (2 s, 2×3 H, C*H*$_3$C=N), 2.72–2.87 [2 poorly defined overlapping sept, 2×1 H, C*H*(CH$_3$)$_2$], 3.88 (s, 3 H, OC*H*$_3$), 5.97 (s, 1 H, α-C*H*), 6.70 (poorly defined d, 1 H), 6.78–6.92 (non-first-order m, 3 H), 6.95–7.01 (non-first-order m, 1 H), 7.02–7.10 (non-first-order m, 1 H), 7.13–7.29 (non-first-order m, 4 H), 7.36 (poorly defined d, 1 H), 7.40 (poorly defined d, 1 H) (2 aromatic C*H*) ppm. $C_{38}H_{45}CrN_3O_4$ (659.79): calcd. C 69.18, H 6.87, Cr 7.88, N 6.37; found C 66.48, H 6.76, Cr 7.62, N 6.02. IR: $\tilde{\nu}$ = 1897, 1802, 1766 [ν(C=O)] 1620, 1597, 1573 [ν(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 304 (br.), 340 [w br. shoulder (π*←n, π*←π)], 469, 540 [shoulder (MLCT)] nm.

1j·Mo(CO)$_3$ (3j): Ligand **1j** (0.529 g, 0.00101 mol), Mo(CO)$_6$ (0.260 g, 0.000985 mol), *n*Bu$_2$O (20 mL) and thf (1 mL) were heated to reflux for 5 h. Orange powder (0.531 g, 77%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 1.08, 1.11, 1.39, 1.43 [4 d, $^3J_{HH}$ = 6.8 Hz, 4×3 H, CH(C*H*$_3$)$_2$], 1.15 [s, 9 H, C(C*H*$_3$)$_3$], 2.24, 2.26 (2 s, 2×3 H, C*H*$_3$C=N), 2.86, 2.91 [2 sept, $^3J_{HH}$ = 6.8 Hz, 2×1 H, C*H*-(CH$_3$)$_2$], 3.89 (s, 3 H, OC*H*$_3$), 5.97 (s, 1 H, α-C*H*), 6.68 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, Ar^{OMe} *o*-C*H*), 6.82 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, Ar^{iPr} *o*-C*H*), 6.87 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, Ar^{OMe} *p*-C*H*), 6.99 (d, $^3J_{HH}$ = 8.3 Hz, 1 H, Ar^{OMe} *m′*-C*H*), 7.06 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, Ar^{OMe} *m*-C*H*), 7.19, 7.24 (2 overlapping t, 2×2 H, Ar^{iPr} *m*- and *p*-C*H*), 7.37, 7.41 (2 d, $^3J_{HH}$ = 7.7 Hz, 2×1 H, Ar^{iPr} *m′*-C*H*) ppm. $C_{38}H_{45}MoN_3O_4$ (703.73): calcd. C 64.86, H 6.45, Mo 13.63, N 5.97; found C 64.07, H 6.60, Mo 13.35, N 5.77. IR: $\tilde{\nu}$ = 1895, 1790, 1776 [*ν*(C=O)] 1615, 1597, 1576 [*ν*(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 293 (π*←n, tailing into π*←π), 444, 505 [shoulder (MLCT)] nm.

1k·Cr(CO)$_3$ (2k): Ligand **1k** (0.205 g, 0.000369 mol), Cr(CO)$_6$ (0.081 g, 0.000368 mol) and *n*Bu$_2$O (10 mL) containing a few drops of thf were heated to reflux for 2.5 h. Black powder (0.129 g, 51%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 0.44 (d, $^3J_{HH}$ = 7.5 Hz, 3 H), 1.03 (d, $^3J_{HH}$ = 6.7 Hz, 3 H), 1.10 (d, $^3J_{HH}$ = 6.7 Hz, 3 H), 1.30 (d, $^3J_{HH}$ = 6.7 Hz, 3 H), 1.45 (d, $^3J_{HH}$ = 6.7 Hz, 3 H), 1.56 (d, $^3J_{HH}$ = 6.7 Hz, 3 H) [6 CH(C*H*$_3$)$_2$], 2.14 (s, 3 H), 2.52 (s, 3 H, C*H*$_3$C=N), 2.30 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H), 2.83 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H), 2.98 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.05 (s, 1 H, α-C*H*), 6.72–6.76 (non-first-order m, 2 H), 7.05–7.10 (non-first-order m, 2 H), 7.18–7.30 (non-first-order m, 7 H), 7.33–7.39 (non-first-order m, 4 H), 7.42–7.47 (non-first-order m, 2 H, aromatic C*H*) ppm. $C_{42}H_{45}CrN_3O_3$ (691.83): calcd. C 72.92, H 6.56, Cr 7.52, N 6.07; found C 72.62, H 6.67, Cr 7.30, N 6.00. IR: $\tilde{\nu}$ = 1893, 1804, 1780 [*ν*(C=O)] 1620, 1597, 1579, 1557 [*ν*(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 290, 360 [shoulder (π*←n, π*←π)], 489, 610 (MLCT) nm.

1k·Mo(CO)$_3$ (3k): Ligand **1k** (0.201 g, 0.000362 mol), Mo(CO)$_6$ (0.095 g, 0.000360 mol) and *n*Bu$_2$O (10 mL) containing a few drops of thf were heated to reflux for 5 h. Very dark purple powder (0.196 g, 74%). ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 0.30 (d, $^3J_{HH}$ = 6.9 Hz, 3 H), 0.83 (d, $^3J_{HH}$ = 6.9 Hz, 3 H), 0.88 (d, $^3J_{HH}$ = 6.9 Hz, 3 H), 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 3 H), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 3 H), 1.31 (d, $^3J_{HH}$ = 6.9 Hz, 3 H) [6 CH(C*H*$_3$)$_2$], 1.91 (s, 3 H), 2.30 (s, 3 H) (2 C*H*$_3$C=N), 2.18 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H), 2.72 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H), 2.84 (sept, $^3J_{HH}$ = 6.9 Hz, 1 H) [3 C*H*(CH$_3$)$_2$], 5.82 (s, 1 H, α-C*H*), 6.46–6.51 (non-first-order m, 2 H), 6.80–6.87 (non-first order m, 2 H), 6.94–7.24 (non-first-order m, 13 H, aromatic C*H*) ppm. $C_{42}H_{45}MoN_3O_3$ (735.78): calcd. C 68.56, H 6.16, Mo 13.04, N 5.71; found C 67.87, H 6.25, Mo 13.01, N 5.59. IR: $\tilde{\nu}$ = 1898, 1802, 1779 [*ν*(C=O)] 1621, 1597, 1581, 1562 [*ν*(C=N)] cm^{-1}. UV/Vis (dichloromethane): λ_{max} = 289, 360 [v. weak shoulder (π*←n, π*←π)], 462, 575 (MLCT) nm.

X-ray Crystallography: Crystals of **1a**–**1c**, **2a** and **3a** suitable for single-crystal X-ray diffraction were grown by vapour diffusion of hexane into dichloromethane (**1a**–**1c**), diethyl ether into chloroform (**2a**), or diethyl ether into acetone (**3a**) solutions. Mounting in oil into an Oxford Instruments Cryostream direct from the mother liquour was employed for **1a**–**1c** and **3a**, whereas crystals of **2a** were isolated and allowed to dry fully, without any detrimental effects to crystal quality, before being mounted in perfluoropolyether oil on the diffractometer. For **1a**–**1c** and **3a**, diffraction intensities were measured with the CCD of a Nonius Kappa diffractometer by using graphite-monochromated Mo-K_α radiation. For **2a**, a Bruker APEX II diffractometer fitted to Station 9.8 of the Daresbury Synchrotron, by using silicon-monochromated Zr-edge radiation, was employed. Data were collected by a mixture of ϕ and ω scans at different θ and κ settings using the program COLLECT.[36] Raw data were processed by using DENZO-SMN[37] to produce *hkl* files, which were solved by using SIR 92[38] and refined by using SHELXL.[39] Two-site disorder in one isopropyl group of **1a** was modeled, and there was a disordered diethyl ether molecule with partial occupancy of the channels in **3a**. Hydrogen atoms from this solvent molecule were not included in the refinement. All non-hydrogen atoms were refined anisotropically, save for the aforementioned disordered solvent atoms; all hydrogen atoms were placed in calculated positions and refined by using a riding model, except where noted in the text. Key crystal, data-collection and refinement data are shown in Table 4. CCDC-699157 (**1a**), -699158 (**1b**), -699159 (**1c**), -699160 (**2a**), and -699161 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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