Dendronized scorpionate complexes of molybdenum in low and high oxidation states†

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Tridentate (L_3) and bidentate (L_2) poly(pyrazolyl)methane ligands (G*n-dend*)$OCH_2C(pz)_3$ (**1–4**) and (G*n-dend*)$CH(3,5\text{-}Me_2pz)_2$ (pz = pyrazol-1-yl) have been used to synthesize the molybdenum(0) complexes $[Mo(CO)_3(L_3)]$ (G0–G3, **5–8**), $[Mo(CO)_4(L_2)]$ (G0–G1, **13–14**), and $[Mo(CO)_3(NCMe)(L_2)]$ (G0, **15**), and the molybdenum(VI) complexes $[MoCl_2O_2(L_2)]$ (**9–12**). The G0–G3 prefixes represent the generation of poly(aryl ether) dendrons in which the metal complexes are embedded. The molecular structures of compounds **13** and **15** have been determined by X-ray diffraction studies and the hydrodynamic radii of tricarbonyl complexes **5–8** calculated by diffusion-ordered NMR spectroscopy (DOSY). Molybdenum(VI) compounds **9–12** have also been evaluated as catalysts for olefin epoxidation, showing comparable but inferior performances than ligand-free $MoCl_2O_2$, probably because of the labile coordination of L_2.

Introduction

Dendrimers functionalized with transition metals have aroused great interest in catalysis, and a large variety of ligands have been used for the fixation of metal complexes at the core, branches or periphery of the dendritic macromolecules.[1–3] We are interested in the way in which the surrounding dendritic arms modulate the properties of metal centers located at the core or focal point of dendritic structures. With this aim, we have undertaken studies on the functionalization of ligands with dendritic substituents [cyclopentadienido,[4] siloxido,[5] diketiminato,[6] phosphine[7] or poly(pyrazol-1-yl)methane[8–10]] and on the behavior of their early and late transition metal complexes as catalysts (polymerization and other carbon–carbon bond-formation reactions).[4,6,7] These studies have been complemented with others to try to understand the organization of the dendritic arms around the metal centers in both the solid state and in solution.[8,9]

The work of Trofimenko in the field of scorpionate chemistry meant that poly(pyrazolyl) ligands rapidly became a very important class of nitrogen donors in modern coordination chemistry,[11] and in the last few years the chemistry of poly(pyrazol-1-yl)alkane complexes, the neutral and isoelectronic counterparts of poly(pyrazol-1-yl)borates, has undergone significant progress.[12,13] This renewed interest has been fuelled, in part, by advances in the syntheses of the ligands themselves[14] and also by their attractive applications in catalysis,[15] bioinorganic chemistry, inorganic and organometallic syntheses, or crystal engineering.[12–20] New metal complexes with unusual structures have been prepared,[16] and major research fields such as heteroscorpionate metal chemistry have grown.[12,17–19]

Despite this rapid development, poly(pyrazolyl) ligands have rarely been used in the chemistry of dendrimers or related compounds. We initially incorporated scorpionate ligands into metallodendrimers by taking advantage of the facile functionalization of the bridging methine carbon atom in tris(pyrazol-1-yl)methane,[8] as first reported by Reger for the preparation of related multitopic ligands and polynuclear compounds containing tris(pyrazolyl)methane units.[21] A different approach has also been reported by Ciriano and Casado for the synthesis of carbosilane dendrimers with peripheral bis- or tris(pyrazolyl)borate ligands coordinated to rhodium.[22] More recently, we have reported that bis(pyrazol-1-yl)methane functionalized at the bridging methylene group with poly(benzyl ether) dendritic wedges (Fréchet dendrons) forms monometallic nickel(II)[9] and palladium(II) complexes.[10]

In a previous report,[8] we showed that sterically demanding substituents bonded directly to the methine bridging carbon of tris(pyrazol-1-yl)methane ligands restrict the arrangement of the pyrazolyl rings and can suppress the coordination capability of these ligands. In order to relax the steric pressure caused by dendritic substituents, we introduced an $–OCH_2–$ spacer between the poly(benzyl ether) dendrons (G*n-dend*) and the methine carbon in the tris(pyrazol-1-yl)methane ligands reported here (Chart 1). The coordination of bis(pyrazol-1-yl)methane ligands is more flexible and Fréchet's dendrons can be linked directly to their methylene bridges, as demonstrated elsewhere,[9,10] even when methyl substituents are introduced in the 3- and 5-positions of the pyrazolyl rings. The synthesis and characterization of series of

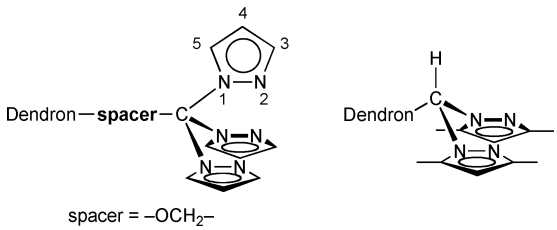

Chart 1

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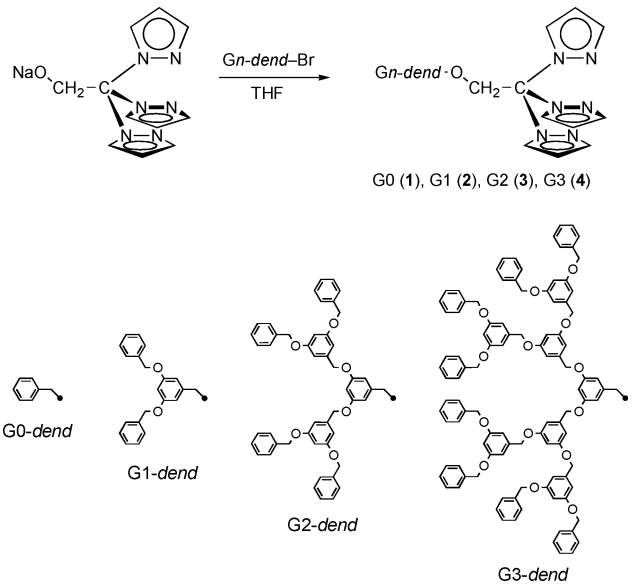
dioxidodichloridomolybdenum(VI) and molybdenum(0) carbonyl complexes of both types of dendritic pyrazolyl ligands is described in this work.

Results and discussion

Synthesis of dendronized tris(pyrazolyl)methane ligands 1–4

Tridentate ligands (G*n*-*dend*)$OCH_2C(pz)_3$ [G*n*-*dend* = poly(benzyl ether) dendron, pz = pyrazol-1-yl, **1–4**] were synthesized by treating the bromoalkanes (G*n*-*dend*)Br (G0–G3) with the alkoxide $NaOCH_2C(pz)_3$ (Scheme 1) and isolated, after appropriate work-up, as white or pale-yellow solids in good yields (>70%, see Experimental for details). They are air-stable in the solid state and in solution. Their solubility in alkanes or diethyl ether is poor and decreases progressively as the generation number (*n*) increases. In contrast, the solubility increases with generation in good solvents such as acetone, THF, or aromatic and chlorinated solvents.

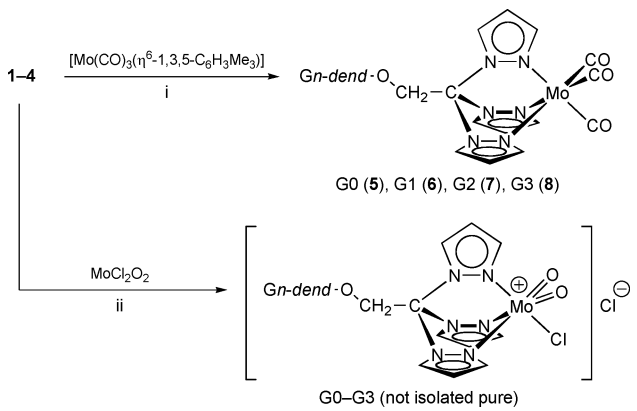


Scheme 1 Synthesis of dendritic ligands **1–4**. Reagents and conditions: (a) 1 equiv. (G*n*-*dend*)Br (*n* = 0, 1, 2, 3), THF, 0 °C; (b) room temperature, overnight.

The three equivalent pyrazolyl rings of compounds **1–4** give rise to three doublets of doublets at about $\delta = 6.3$ (H^4), 7.4 (H^5), and 7.6 ppm (H^3) in the ^1H NMR spectra and three singlets at about $\delta = 106$ (C^4), 131 (C^5), and 141 ppm (C^3) in the $^{13}C\{^1H\}$ NMR spectra (See Chart 1 for the numbering scheme of the pyrazolyl rings). The methine carbon [$C(pz)_3$] is found at $\delta = 90$ ppm and the protons attached to the neighboring methylene group appear as a singlet at around $\delta = 5.1$ ppm. The protons of the dendritic moieties give sets of resonances in the three regions characteristic for this type of poly(benzyl ether) dendrons,[9,10,23] namely multiplets at $\delta = 7.2$–7.4 ppm for the terminal phenyl groups (Ph), a doublet and a triplet at $\delta = 6.4$–6.6 ppm for each layer of internal aryl groups (Ar), and a singlet at $\delta = 4.5$–4.9 ppm for each generation of $–CH_2O–$ groups. The $^{13}C\{^1H\}$ NMR spectra of compounds **1–4** also show a set of resonances for each layer, the relative intensities of which increase on going from the focal point to the periphery of the dendron. The most significant band found in the IR spectra of these ligands is an absorption assigned to the asymmetric stretching of the C=N bond at around 1520 cm^{-1}, together with clearly visible bands assigned to the C=C and C–O–C vibrations (**2–4**). Peaks with isotope distributions that match the calculated patterns for the molecular fragments plus sodium or potassium cations were observed by ESI^+-TOF mass spectrometry.

Synthesis of molybdenum complexes

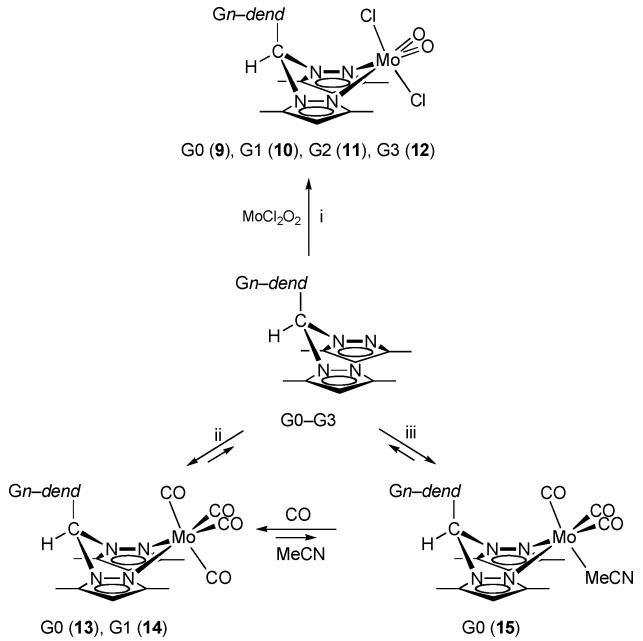
The carbonyl molybdenum(0) complexes [$Mo(CO)_3${(G*n*-*dend*)$OCH_2C(pz)_3$}] (**5–8**, Scheme 2, i) were isolated as yellowish solids in good yields (> 83%) after treatment of one equivalent of the tris(pyrazolyl)methane ligands **1–4** with [$Mo(CO)_3(\eta^6$-1,3,5-$C_6H_3Me_3$)] in THF. The synthesis of the related complexes [$Mo(CO)_3${$HC(pz)_3$}] with tris(pyrazol-1-yl)methane or tris(3,5-dimethylpyrazol-1-yl)methane ligands not substituted at the bridging methine carbon was originally reported by Trofimenko starting from molybdenum hexacarbonyl.[24,25] Complexes **5–8** are insoluble in alkanes or diethyl ether, partially soluble in chlorinated or aromatic solvents, and soluble in acetone and THF. Their solubility tends to increase with generation as a consequence of the increase in the number of terminal groups at the molecular surface of the dendritic wedge. They are relatively stable to air in the solid state but decompose to brown materials after several days.



Scheme 2 Synthesis of molybdenum compounds with dendritic tris(pyrazolyl)methane ligands. Conditions: (i) 1 equiv. [$Mo(CO)_3(\eta^6$-1,3,5-$C_6H_3Me_3$)], THF, room temperature, 5 h. (ii) 1 equiv. [$MoCl_2O_2$], THF, room temperature, 1 h.

Several oxidomolybdenum(VI) complexes have proven to be useful catalysts for the epoxidation of olefins with hydroperoxides. For example, Kühn, Romão and coworkers have synthesized complexes of formula [$MoXO_2${$HC(pz)_3$}]X (X = Cl, Br) starting from [$MoO_2X_2(THF)_2$].[26] However, our attempts to isolate the related complexes [$MoClO_2${(G*n*-*dend*)$OCH_2C(pz)_3$}]Cl under similar conditions failed to give pure products (Scheme 2, ii). Thus, the treatment of ligands **1–4** with [$MoCl_2O_2$] or [$MoCl_2O_2L_2$] (L = THF or DMSO) in THF at room temperature resulted in the precipitation of white, air-sensitive solids containing the expected products spectroscopically almost pure (see Experimental for ^1H NMR data). These impure solids were found to be soluble in chlorinated solvents and insoluble in diethyl ether, although all attempts to obtain analytically pure samples failed or resulted in decomposition.

As an alternative to the preceding cationic molybdenum(VI) complexes, neutral dioxido compounds of general formula $[MoCl_2O_2(L_2)]$ can be prepared with bidentate instead of tridentate pyrazolylmethane ligands.[26] Thus, complexes **9–12** were isolated as yellowish solids in good yields (77–89%) by treatment of the dendritic bis(pyrazolyl)methane ligands (G*n*-*dend*)CH(3,5-$Me_2pz)_2$ (3,5-Me_2pz = 3,5-dimethylpyrazol-1-yl)[9] with $[MoCl_2O_2]$ in THF (Scheme 3, i). Complexes **9–12** are rather unstable to air and moisture in both the solid state and in solution. They are insoluble in alkanes or diethyl ether, partially soluble in chlorinated or aromatic solvents, and soluble in THF.



Scheme 3 Synthesis of molybdenum compounds with dendritic bis(pyrazolyl)methane ligands. Conditions: (i) 1 equiv. $[MoCl_2O_2]$, THF, room temperature, 1 h. (ii) 1 equiv. $[Mo(CO)_6]$, toluene, 55 °C, 4 (**13**) or 7 (**14**) days. (iii) 1 equiv. $[Mo(CO)_3(NCMe)_3]$, toluene, room temperature, 4 h.

Bis(pyrazolyl)methane ligands form molybdenum(0) carbonyl complexes of general formula $[M(CO)_n\{RR'C(pz)_2\}]$ (n = 3 or 4).[27,28] Such compounds are usually prepared by heating a solution of the free ligands and $Mo(CO)_6$ for several hours at temperatures higher than 70–80 °C in solvents such as toluene, DME, or acetonitrile. The preparation of the dendritic complexes $[Mo(CO)_n\{$(G*n*-*dend*)CH(3,5-$Me_2pz)_2\}]$ was, however, not that straightforward. Direct combination of $Mo(CO)_6$ with the respective (G*n*-*dend*)CH(3,5-$Me_2pz)_2$ ligands in warm toluene afforded compounds **13** (G0) and **14** (G1) in approximately 75% yields (Scheme 3, ii), whereas almost complete decomposition was observed in DME or THF. The reaction in toluene had to be conducted at 55 °C because of the poor thermal stability of the reaction mixtures, which gradually became dark at higher temperatures (≥ 70 °C). The reaction proceeded more slowly at these lower temperatures and required several days for completion. Periodic removal of the CO evolved under vacuum also proved necessary to avoid its recoordination. In contrast, two of the three acetonitrile ligands of $[Mo(CO)_3(NCMe)_3]$ were replaced by the G0 ligand $PhCH_2CH(3,5\text{-}Me_2pz)_2\}$ in toluene or benzene in a matter of hours at room temperature (Scheme 3, iii). This reaction led to pure $[Mo(CO)_3(NCMe)\{PhCH_2CH(3,5\text{-}Me_2pz)_2\}]$ (**15**) in good yields (80%) thanks to the precipitation of the complex from the reaction solution. However, treatment of $PhCH_2CH(3,5\text{-}Me_2pz)_2$ with $[Mo(CO)_3(NCMe)_3]$, $[Mo(CO)_3(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$, or $[Mo(CO)_6]$ in acetonitrile or in other polar solvents such as THF or acetone in the presence of added acetonitrile led to product mixtures containing varying amounts of **13**, **15**, and the free ligand. Compounds **13–15** are insoluble in alkanes, diethyl ether, aromatic solvents, and soluble in acetone or acetonitrile; they decompose quickly in THF solution. They are unstable to air and moisture in the solid state and in solution. Moreover, solutions of pure compound **15** in [D_6]acetone or [D_3]acetonitrile change over time to give mixtures of **15**, **13**, and free ligand with relative compositions 6 : 2 : 1 (acetone) or 4 : 1 : 1 (acetonitrile) after 10 min, stabilizing after about 16 h at 2 : 3 : 1 (acetone) or 4 : 3 : 1 (acetonitrile) ratios. These solutions were found to contain only **13** and free ligand [and probably $Mo(CO)_6$] after bubbling CO gas through them briefly. The initial composition could be slowly recovered after replacing the CO with an argon atmosphere. Similarly, solutions of compound **13** were transformed into the same mixture in [D_3]acetonitrile or in [D_6]acetone and MeCN. It appears that compound **13** is more stable than **15** and that the CO/MeCN scrambling process, which is promoted by polar solvents,[29] facilitates the equilibrium process, with concomitant formation of unidentified Mo species and free ligand. It has been suggested that the moderate stability of the bis(pyrazolyl)methane coordination in $[M(CO)_4\{CH_2(pz)_2\}]$ (M = Cr, Mo, and W) complexes is partly a consequence of the differences in the conformational energy between the coordinated and free ligand.[27a] The steric repulsion between the G*n*-*dend* and pz-Me^5 groups increases the rigidity of the metallacycle in the complexes described here (see NMR and X-ray discussion) and probably makes the coordination of the (G*n*-*dend*)CH(3,5-$Me_2pz)_2$ ligands even more unstable than that of the unsubstituted $CH_2(pz)_2$ ligand. Shiu has shown that prolonged thermolysis of $[Mo(CO)_4\{(C_6H_5)CH(3,5\text{-}Me_2pz)_2\}]$ in DME gives $[Mo(CO)_3\{(\eta^2\text{-}C_6H_5)CH(3,5\text{-}Me_2pz)_2\}]$ by decarbonylation and weak intramolecular η^2-binding of the phenyl group to the metal center.[28b] A simple Cochrane molecular model suggests that such an η^2-binding is even more favorable for the benzyl group of complex **13**. All attempts to promote a similar transformation in **13** at reflux or by warming samples of the complex in a sealed ampoule under vacuum in DME, THF, acetone, or toluene resulted, however in mixtures of decomposition products and unreacted **13**.

All the reported complexes were characterized by ^1H and $^{13}C\{^1H\}$ NMR and IR spectroscopy, elemental analysis, and mass spectrometry. Coordination of the ligands to the molybdenum atom only produces significant shifts in the proton and carbon-13 resonances of the nuclei close to the metal center, especially those in the 3-position of the pyrazolyl ring ($\Delta\delta$ = +0.8, +0.7, and +0.5 ppm for H^3 and +5, +10, and +8 ppm for C^3 in **5–8**, **9–12**, and **13–15**, respectively).‡ The chemical shifts of most of

‡ Ligand (G0-*dend*)CH(3,5-$Me_2pz)_2$: ^1H NMR (C_6D_6): δ 1.97 (s, 6 H, pz-Me^3), 2.19 (s, 6 H, pz-Me^5), 3.96 (d, $J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 5.57 (s, 2 H, pz-H^4), 6.38 (t, $J_{H,H}$ = 7.2 Hz, 1 H, CH), 6.9–7.0 ppm (m, 5 H, Ph). ^1H NMR ([D_6]acetone): δ 2.08 (s, 6 H, pz-Me^3), 2.10 (s, 6 H, pz-Me^5), 3.87 (d,

the nuclei located at the core of dendrons are shifted progressively upfield with increasing generation, from G0 to G3, in the metal complexes described here. For example, the chemical shift of the $CH_2C(pz)_3$ protons in **5–8** moves from $\delta = 5.87$ ppm in **5** to $\delta =$ 5.82, 5.80, and 5.77 ppm in **6–8**, respectively, the chemical shift of H^4 moves from $\delta = 6.47$ ppm in **5** to $\delta = 6.45$, 6.42 and 6.40 ppm in **6–8**, respectively, and that of H^3 moves from $\delta = 8.42$ ppm in **5** to $\delta = 8.38$, 8.36, and 8.32 ppm in **6–8**, respectively. Likewise, on going from **9** to **11** the chemical shift of Me^5 follows the sequence $\delta = 2.10$, 2.05, and 2.01 ppm, that of Me^3 the sequence $\delta = 2.74$, 2.73, and 2.71 ppm, that of pz-H^4 the sequence $\delta = 6.47$, 6.45, and 6.42 ppm, and that of CH(3,5-Me_2pz)$_2$ the sequence $\delta = 6.09$, 6.00, and 5.98 ppm. This small but consistent effect might be due to an increased shielding at the focal point caused by the presence of an increasing number of aryl groups.

The pyrazolyl rings of complexes **5–15** give rise to a unique set of proton and carbon-13 resonances at room temperature. This is indicative of apparent C_{3v} (**5–8**) or C_s (**9–15**) symmetry in solution and is also in accordance with the single ^{13}C resonances observed for the carbonyl groups in complexes **5–8** ($\delta = 230$ ppm). In contrast, the ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes $[MoClO_2\{(Gn\text{-}dend)OCH_2C(pz)_3\}]Cl$ show the existence of two different pyrazolyl groups in a 2 : 1 ratio assigned, respectively, to the rings *trans* to the oxido and *trans* to the chlorido ligands of a rigidly coordinated tris(pyrazolyl)methane ligand (see Scheme 2).

The carbonyl groups of complexes **13** and **14** give rise to three ^{13}C resonances at $\delta = 220$, 208, and 207 ppm, respectively. Because carbonyl groups are π-acceptors, the low-field signal was assigned to the carbonyl groups located *trans* to the pyrazolyl groups and the two higher field resonances to the mutually *trans* CO ligands. The chemical inequivalence of the latter is coherent with the predominance in solution of a boat conformation for the bis(pyrazolyl) metallacycle, similar to that found in the solid state, with no boat-to-boat conformational exchange (see below and Fig. 1).[8–10,28c,30] The number of CO resonances reduces to two for **15** ($\delta = 228$, 207 ppm), as expected, as the coordinated acetonitrile replaces one of the two mutually *trans* carbonyl groups in **13**.

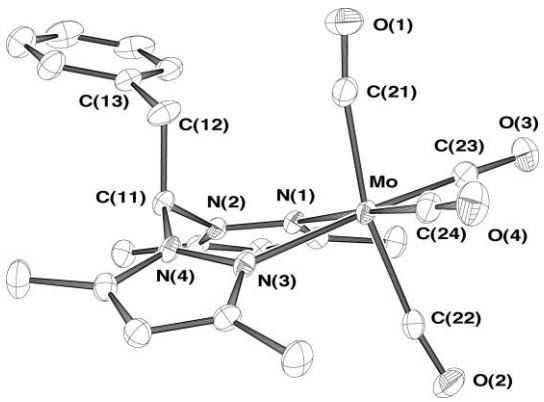


Fig. 1 ORTEP diagram of the structure of compound **13** with thermal ellipsoids at 50% probability.

$J_{H,H} = 7.2$ Hz, 2 H, CH_2), 5.72 (s, 2 H, pz-H^4), 6.42 (t, $J_{H,H} = 7.2$ Hz, 1 H, CH), 7.15–7.25 ppm (m, 5 H, Ph).

The IR spectra were recorded for all the new complexes in KBr pellets and show a ν_{as}(C=N) absorption at around 1520 (**5–8**) or 1560 cm^{-1} (**9–15**). The number of IR bands in the region of the CO stretching vibrations is in agreement with the proposed structures, namely two absorptions for the tricarbonyl compounds **5–8** or **15** of approximate C_{3v} symmetry (A_1 + E) and four absorptions for the tetracarbonyl complexes **13** and **14** of local C_{2v} symmetry (2 A_1, B_1, and B_2 modes). Two strong absorptions are observed in the ν(Mo=O) region for complexes **9–12** at about 950 (asymmetric) and 920 cm^{-1} (symmetric), in agreement with a *cis*-$[MoO_2]^{2+}$ geometry.

The molecular ions of complexes **5–9** were detected in the ESI^+-TOF mass spectra with the expected isotopic distributions, although often with hydrogen or alkali-metal cations incorporated. The bis(pyrazolyl)methane complexes **9**, **10**, and **12** only gave peaks corresponding to the free ligands, whereas fragments derived from the molecular ions by the loss of one or more CO groups (or acetonitrile for **15**) were observed in the mass spectra of the carbonyl compounds **13–15**.

We recently published several studies dealing with the conformational disposition of poly(benzyl ether) dendrons around the metal center in bis(pyrazolyl)methane complexes of nickel(II)[9] and palladium(II).[10] These studies are relevant on account of the role that dendrimers can play in the confinement of active centers in catalytic processes.[3] Our studies were based on solid-state structures determined by single-crystal X-ray diffraction and on nuclear longitudinal relaxation rates obtained in solution for molecules with paramagnetic metal centers. In addition to its conventional role of providing detailed information about the local environment of active nuclei, NMR spectroscopy is also a powerful tool for the study of overall molecular properties. Translational motion can be studied in a practical way by diffusion NMR spectroscopy.[31] The hydrodynamic radii, R_H, can be calculated from the diffusion coefficient of a certain molecular species using the Stokes–Einstein equation (eqn (1)), where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solution.

$$R_H = \frac{k_B T}{6\pi\eta D} \quad (1)$$

We measured the self-diffusion coefficients of dendrimers **5–8** in deuterated acetone at 25 °C using high-resolution diffusion-ordered spectroscopy (DOSY, see Experimental for details).[32] The values obtained were 13.4×10^{-10} (G0), 11.3×10^{-10} (G1), 9.1×10^{-10} (G2), and 6.5×10^{-10} m^2 s^{-1} (G3), respectively. The hydrodynamic radii of complexes **5–8** were calculated to be 5.0 (G0), 5.9 (G1), 7.4 (G2), and 10.2 Å (G3) from these measurements. Eqn (1) assumes that sample molecules are spherical and much larger than the solvent, therefore the calculated radii should be considered as estimates. Riley *et al.*[33] have reported R_H values for similar poly(benzyl ether) dendrons with pyrene units at their focal point in good solvents, where the dendritic structures tend to be extended, and in bad solvents, which favor the collapse of the structure. Taking into account the larger size of the tris(pyrazolyl)molybdenum tricarbonyl complex, the radii of **5–8** in deuterated acetone are in good agreement with those reported for the pyrene compounds in a good solvent such as THF (3.7 (G0), 4.9 (G1), 6.2 (G2), and 10 Å (G3)].

Structures of $[Mo(CO)_4\{PhCH_2CH(3,5\text{-}Me_2pz)_2\}]$ (13) and $[Mo(CO)_3(NCMe)\{PhCH_2CH(3,5\text{-}Me_2pz)_2\}]$ (15)

Fig. 1 and 2 show ORTEP representations of the molecular structure of compounds **13** and **15**, respectively, as determined in the solid state by single-crystal X-ray diffraction studies; the relevant structural data are given in Table 1.

The molecular structure of **13** (Fig. 1) shows a six-coordinate central molybdenum atom in a distorted octahedral geometry with the bis(pyrazolyl)methane group acting as a bidentate chelating ligand. The bond angles around the metal centre are in the range 166.5(1)–177.0(1)° for atoms located *trans* each other and 84.0(1)–99.9(1)° for those in *cis* positions, with the exception of the acute angle defined by the pyrazolyl nitrogen atoms [79.2(1)°]. The average Mo–N [2.314(2) Å] and Mo–C [2.004(3) Å] bond distances fall in the usual range,[28,34] with slightly longer distances to the carbonyl carbons that are mutually *trans*, as would be expected. These carbonyl groups are somewhat tilted toward the axis bisecting the Mo–CO(*cis*) bonds: the angle C(21)–Mo–C(22) is 166.5(1)°, while the dihedral angle defined by the N(1)–Mo–N(3) and C(21)–Mo–C(22) planes is almost a right angle [89.7(1)°]. This distortion is most likely due to the steric repulsions between the *trans* carbonyl groups and the bis(pyrazolyl)methane ligand. The metallacycle adopts a boat conformation, as typically found in related complexes,[28,34] and the benzyl group attached to the methine carbon C(11) occupies the axial position. The same arrangement has been found in palladium(II),[8,10,30] nickel(II),[9] and molybdenum(0)[28c] complexes with $RCH(3,5\text{-}Me_2pz)_2$ ligands (R = phenyl, benzyl, pyridyl, or dendrons) and has been ascribed to the steric hindrance that would arise in the equatorial location with the adjacent methyl groups at the 5-position of the pyrazolyl rings. This steric repulsion between the R and pz-Me[5] groups confers rigidity on the metallacycle and explains the absence of a boat-to-boat conformational exchange in solution (see NMR discussion). The boat conformation is less pronounced on the side of the metal centre than on that of the carbon bridge, and the pyrazolyl rings show a saddlebag-type disposition with a dihedral angle of 48.6(1)°. The benzyl group is orientated asymmetrically towards the hemi-space that contains the N(1)–N(2) pyrazolyl ring, with a dihedral angle defined by the C(12)–C(13) bond and the Mo···C(11) molecular axis of 137.4°.

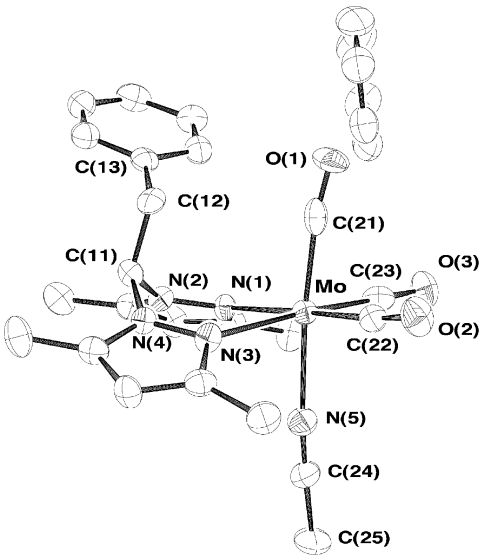


Fig. 2 ORTEP diagram of the structure of compound **15**·C_6D_6 (enantiomer a) with thermal ellipsoids at 50% probability.

Table 1 Bond lengths [Å] and angles [°] for compounds **13** and **15**

13		**15** (enantiomer a)	
Mo–C(21)	2.044(3)	Mo–C(21)	1.967(9)
Mo–C(24)	1.954(3)	Mo–C(22)	1.934(7)
Mo–C(23)	1.963(3)	Mo–C(23)	1.916(8)
Mo–C(22)	2.056(0)	Mo–N(5)	2.278(7)
Mo–N(1)	2.320(2)	Mo–N(1)	2.328(6)
Mo–N(3)	2.308(2)	Mo–N(3)	2.327(6)
C(21)–Mo–C(23)	84.35(11)	C(21)–Mo–C(23)	83.0(3)
C(21)–Mo–C(24)	83.95(11)	C(21)–Mo–C(22)	81.6(3)
C(21)–Mo–C(22)	166.53(10)	C(21)–Mo–N(5)	174.8(3)
C(21)–Mo–N(1)	97.70(9)	C(21)–Mo–N(1)	99.6(2)
C(21)–Mo–N(3)	98.65(9)	C(21)–Mo–N(3)	101.7(3)
C(24)–Mo–N(1)	175.37(9)	C(22)–Mo–N(1)	177.6(3)
C(24)–M–N(3)	96.24(9)	C(22)–Mo–N(3)	99.1(3)
C(23)–Mo–C(24)	84.51(11)	C(23)–Mo–C(22)	83.3(3)
C(23)–Mo–N(1)	99.94(9)	C(23)–Mo–N(1)	98.9(3)
C(23)–Mo–N(3)	176.96(9)	C(23)–Mo–N(3)	175.0(3)
C(22)–Mo–C(23)	85.33(11)	N(5)–Mo–C(23)	92.0(0)
C(22)–Mo–C(24)	86.47(11)	N(5)–Mo–C(22)	96.4(3)
C(22)–Mo–N(1)	92.58(9)	N(5)–Mo–N(1)	82.6(2)
C(22)–Mo–N(3)	91.77(9)	N(5)–Mo–N(3)	83.4(2)
N(1)–Mo–N(3)	79.25(7)	N(1)–Mo–N(3)	78.6(2)
Mo–C(21)–O(1)	170.4(2)	Mo–C(21)–O(1)	171.2(6)
Mo–C(22)–O(2)	171.2(2)	Mo–N(5)–C(24)	173.6(6)
Mo–C(23)–O(3)	175.8(2)	Mo–C(23)–O(3)	177.1(6)
Mo–C(24)–O(4)	177.6(2)	Mo–C(22)–O(2)	174.7(7)
		N(5)–C(24)–C(25)	178.0(9)

Complex **15** was crystallized from C_6D_6. The asymmetric part of the unit cell consists of two enantiomers (a and b) with similar bond parameters—they differ only in the relative orientation of the benzyl group—and two crystallization benzene molecules. Fig. 2 and Table 1 concern the enantiomer adduct **15a**·C_6D_6. The molecular structure of **15** resembles that of **13** but with the CO group situated *anti* to the phenyl ring replaced by an acetonitrile ligand. Similar distortions are observed in the octahedral geometry around the metal center, with bond angles ranging from 177.6(3)° to 174.8(3)° for the atoms located *trans* or from 101.7(3)° to 81.46(3)° for those located *cis*, and an N(1)–Mo–N(3) angle of 78.6(2)°. The Mo–N(pz) [2.328(6) Å] and Mo–CO(mean) [1.939(8) Å] bond distances are slightly longer and shorter, respectively, than those found in **13**, and the distances to the carbonyl carbons *trans* to the chelate ligand are again slightly shorter. The acetonitrile ligand is coordinated in a rather linear mode [Mo–N(5)–C(24) = 173.6(6)°, N(5)–C(24)–C(25) = 178.0(9)°] with an Mo–N(5) distance of 2.278(7) Å. The carbonyl group *trans* to acetonitrile is the most affected by the steric repulsion between the ligands, being tilted toward the other carbonyl ligands. The metallacycle in **15** adopts a similar boat conformation to that described for **13**. The dihedral angle between the pyrazolyl rings is 50.2(3)°, and the asymmetric positioning of the benzyl group is defined by the dihedral angle C(13)–C(12)–C(11)···Mo of 110.9°.

Catalytic oxidation using molybdenum(VI) complexes 9–12

We tested these compounds as catalyst precursors for the epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide under the

conditions described by Romão and coworkers.[26] The reactions proved to be highly exothermic under these conditions, with conversions of the olefin to the corresponding epoxide of more than 90% in 10 min. Complete conversion were reached in less than 30 min without significant differences between the four dendritic complexes. $[MoCl_2O_2]$ showed the same performance as the bis(pyrazolyl) complexes in the absence of ligands.

We then reduced the Mo loading from 1 mol% to 0.05 mol% and monitored the reaction under these milder conditions by GC (see Experimental for further details). The catalytic profile was again almost independent of the dendritic generation of the catalyst (Fig. 3), and only the G0 compound **9** showed a slightly inferior initial turnover frequency (5760 h^{-1} compared with approx. 11 000 h^{-1} for **10–12** in the first 5 min of reaction). Surprisingly, ligand-free $MoCl_2O_2$ proved to be more active (14 640 h^{-1}) than any of the bis(pyrazolyl) complexes and afforded 100% conversion after 5 h (compared with 92–96% for **9–12**).

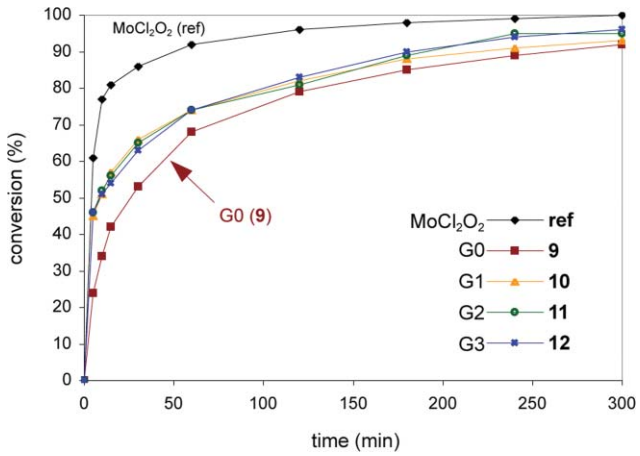


Fig. 3 Catalytic profile in the oxidation of *cis*-cyclooctene for **9–12**, and the reference compound $MoCl_2O_2$.

We have shown above that bidentate (G*n-dend*)$CH(3,5\text{-}Me_2pz)_2$ ligands are more prone to dissociate from the metal center due to steric conformational restraints. We can speculate that, under catalytic conditions, the ligand dissociates quickly to afford more active species, therefore the less congested G0 ligand is initially less active and the ligand-free MoO_2Cl_2 precursor has a higher initial TOF, although the differences are small. Colbran and coworkers have recently studied alkene epoxidation using a dioxo(pentaarylcyclopentadienido)molybdenum(VI) complex and postulated that, in spite of the stability of the cyclopentadienido coordination, decomposition to a much more active non-cyclopentadienido-containing catalyst occurs as the reaction proceeds.[35] The low binding constants of bis(pyrazolyl)methane ligands has been argued previously by Jordan to explain the performance of bis(pyrazolyl)methanepalladium(II) compounds in ethylene polymerization,[36] and also explains the behavior observed by us for nickel(II) complexes containing similar dendritic ligands.[9]

Conclusions

We have reported the synthesis of molybdenum(0) and molybdenum(VI) complexes with bis- and tris(pyrazolyl)methane ligands embedded in poly(benzyl ether) dendrons of up to the third generation. The presence of an $–OCH_2–$ spacer between the dendritic wedge and the $C(pz)_3$ moiety permits the tridentate coordination of the tris(pyrazolyl) ligands, as demonstrated by the straightforward preparation of their molybdenum(0) tricarbonyl complexes.

While the products resulting from the reaction of $[Mo_2Cl_2O_2]$ with the tridentate ligands could not be isolated in a pure form, the synthesis of the bis(pyrazolyl)methane complexes worked well. Furthermore, compounds $[Mo(CO)_4\{Gn\text{-}(dend)CH(3,5\text{-}Me_2pz)_2\}]$ [G*n* = G0 (**13**), G1 (**14**)] and $[Mo(CO)_3\{G0\text{-}(dend)CH(3,5\text{-}Me_2pz)_2\}MeCN]$ (**15**) were isolated in good yields as substances that are fairly unstable in solution. The characterization of these bidentate metal complexes in solution by NMR spectroscopy and of **13** and **15** in the solid state by X-ray diffraction is consistent with the conformational rigidity of the coordinated bis(pyrazolyl)methane ligands, which could explain the tendency of some of them to dissociate. The catalytic behavior of complexes **9–12** found in the epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide is almost independent of the dendron-generation, being slightly inferior in activity than the ligand-free $MoCl_2O_2$ parent compound.

Experimental

General remarks

All operations were performed under argon using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. The compounds $NaOCH_2C(pz)_3$,[8] $[Mo(CO)_3(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$,[37] $[Mo(CO)_3(NCMe)_3]$,[38] (G*n-dend*)Br (G1–G3),[23] and (G*n-dend*)-$CH(3,5\text{-}Me_2pz)_2$ (G0–G3)[9] were prepared according to literature procedures. Solvents were previously dried and distilled under argon as described elsewhere.[39] NMR spectra were recorded with Varian Unity 500+, VR-300, or 200 spectrometers. Chemical shifts (δ) are reported in ppm relative to $SiMe_4$, and were referenced with respect to ^{13}C and residual ^{1}H resonances of the deuterated solvents. Coupling constants (J) are given in Hz. The following abbreviations/notations are used: Ph refers to aromatic ring of terminal benzyl groups, Ar to internal rings of benzyl ethers, and *ipso* refers to the first ring-position on going from the di- or tridentate pyrazolyl ligand. The numbering scheme for the pyrazolyl ring atoms is given in Chart 1. IR spectra were recorded with a Perkin-Elmer FT-IR Spectrum-2000 spectrophotometer. The Microanalytical Laboratories of the University of Alcalá performed the elemental analyses with a Heraeus CHN–O-Rapid microanalyzer and the mass spectra with a Thermoquest-Finnigan Automass Multi or an AGILENT 6210 LC/MS TOF Multi (ESI) mass spectrometer. The products of catalysis were analyzed with a CHROMPACK CP 9001 gas chromatograph using a fused silica HP-INNOWax capillary column (15 m, 0.25 mm i.d., 0.25 μm df) under the following conditions: injector and detector temperature: 250 °C; oven temperature program: 140 °C isotherm.

General procedure for the preparation of (G*n-dend*)$OCH_2C(pz)_3$ (1–4). The corresponding benzyl wedge (G*n-dend*)Br (n = 0, 1, 2, 3) and $NaOCH_2C(pz)_3$ were combined in THF (15 mL) at 0 °C. The temperature was subsequently allowed to rise to room temperature and stirring was continued overnight. The resulting reaction mixture was filtered through Celite using a cannula-filter, the solvent was removed *in vacuo*, and the crude residue treated as

described individually below to give the title compounds as white (**1–3**) or pale-yellow (**4**) solids.

(G0-*dend*)OCH$_2$C(pz)$_3$ (1). PhCH$_2$Br (0.30 mL, 2.5 mmol) and NaOCH$_2$C(pz)$_3$ (544 mg, 2.04 mmol). Recrystallized from pentane. Yield: 616 mg (90%). Anal. Calc. for $C_{18}H_{18}N_6O$ (334.38): C, 64.66; H, 5.43; N, 25.13%. Found: C, 64.12; H, 5.43; N, 24.71%. ^{1}H NMR (CDCl$_3$): δ 4.50 (s, 2 H, PhCH$_2$O), 5.12 [s, 2 H, CH$_2$C(pz)$_3$], 6.32 (dd, $J_{H,H}$ = 1.5, 2.5 Hz, 3 H, pz-H^4), 7.14–7.20 (m, 2 H, Ph), 7.25–7.34 (m, 3 H, Ph), 7.42 (d, $J_{H,H}$ = 2.5 Hz, 3 H, pz-H^5), 7.64 ppm (d, $J_{H,H}$ = 1.5 Hz, 3 H, pz-H^3). ^{1}H NMR ([D$_6$]acetone): δ 4.55 (s, 2 H, PhCH$_2$O), 5.11 [s, 2 H, CH$_2$C(pz)$_3$], 6.34 (dd, $J_{H,H}$ = 1.5, 2.5 Hz, 3 H, pz-H^4), 7.20–7.35 (m, 5 H, Ph), 7.49 (d, $J_{H,H}$ = 2.5 Hz, 3 H, pz-H^5), 7.59 (d, $J_{H,H}$ = 1.5 Hz, 3 H, pz-H^3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 73.4 and 74.1 (CH$_2$OCH$_2$), 89.8 [C(pz)$_3$], 106.5 (pz-C^4), 127.9 (*p*-Ph), 127.7 and 128.4 (*o*- and *m*-Ph), 130.9 (pz-C^5), 137.0 (*ipso*-Ph), 141.4 ppm (pz-C^3). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ 73.9 and 74.3 (-CH$_2$OCH$_2$-), 90.6 [C(pz)$_3$], 106.8 (pz-C^4), 128.6 (*p*-Ph), 128.5 and 129.1 (*o*- and *m*-Ph), 131.7 (pz-C^5), 138.5 (*ipso*-Ph), 141.5 ppm (pz-C^3). IR (KBr pellet): ν 1519 (s, C=N), 1620 (m, C=C), 1451 cm^{-1} (s, C=C). MS (ESI$^+$-TOF in CH$_2$Cl$_2$/MeOH/NH$_4$HCOO 5 mM): *m*/*z* 357.14 [M + Na]$^+$, 267.31 [M − pz]$^+$, 199.23 [M − 2 pz − H]$^+$.

(G1-*dend*)OCH$_2$C(pz)$_3$ (2). (G1-*dend*)Br (766 mg, 2.00 mmol) and NaOCH$_2$C(pz)$_3$ (532 mg, 2.00 mmol). Recrystallized by dissolving the crude reaction mixture in the minimum volume of diethyl ether, adding hexane, and stirring for several hours. Yield: 787 mg (72%). Anal. Calc. for $C_{32}H_{30}N_6O_3$ (546.63): C, 70.31; H, 5.53; N, 15.37%. Found: C, 70.31; H, 5.34; N, 15.07%. ^{1}H NMR (CDCl$_3$): δ 4.44 (s, 2 H, ArCH$_2$O), 4.97 (s, 4 H, PhCH$_2$O), 5.11 [s, 2 H, CH$_2$C(pz)$_3$], 6.31 (dd, $J_{H,H}$ = 1.5, 2.4 Hz, 3 H, pz-H^4), 6.43 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H, *o*-Ar), 6.51 (t, $^4J_{H,H}$ = 2.1 Hz, 1 H, *p*-Ar), 7.30–7.38 (m, 10 H, Ph), 7.40 (d, $J_{H,H}$ = 2.4 Hz, 3 H, pz-H^5), 7.63 ppm (d, $J_{H,H}$ = 1.5 Hz, 3 H, pz-H^3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 70.1 (PhCH$_2$O), 73.4 and 74.0 (-CH$_2$OCH$_2$-), 89.8 [C(pz)$_3$], 101.6 (*p*-Ar), 106.5 (pz-C^4), 106.6 (*o*-Ar), 128.0 (*p*-Ph), 127.5 and 128.6 (*o*- and *m*-Ph), 130.9 (pz-C^5), 136.7 (*ipso*-Ph), 139.5 (*ipso*-Ar), 141.3 (pz-C^3), 160.0 ppm (*m*-Ar). IR (KBr pellet): ν 1515 (m, C=N), 1595 and 1452 (s, C=C), 1297 (s, C–O–C$_{as}$), 1165 and 1028 cm^{-1} (s, C–O–C$_s$). MS (ESI$^+$-TOF in CH$_2$Cl$_2$/MeOH/NH$_4$HCOO 5 mM): *m*/*z* 1115.47 [M$_2$ + Na]$^+$, 569.23 [M + Na]$^+$, 411.18 [M − 2 pz − H]$^+$.

(G2-*dend*)OCH$_2$C(pz)$_3$ (3). (G2-*dend*)Br (500 mg, 0.62 mmol) and NaOCH$_2$C(pz)$_3$ (165 mg, 0.62 mmol). The resulting yellow oil was triturated with diethyl ether to give a solid. Yield: 518 mg (86%). Anal. Calc. for $C_{60}H_{54}N_6O_7$ (971.12): C, 74.21; H, 5.60; N, 8.65%. Found: C, 74.00; H, 5.73; N, 8.14%. ^{1}H NMR (CDCl$_3$): δ 4.43 (s, 2 H, G0-ArCH$_2$O), 4.89 (s, 4 H, G1-ArCH$_2$O), 5.01 (s, 8 H, PhCH$_2$O), 5.11 [s, 2 H, CH$_2$C(pz)$_3$], 6.29 (dd, $J_{H,H}$ = 1.5, 2.0 Hz, 3 H, pz-H^4), 6.40 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H, G0-*o*-Ar), 6.48 (t, $^4J_{H,H}$ = 1.8 Hz, 1 H, G0-*p*-Ar), 6.55 (t, $^4J_{H,H}$ = 2.1 Hz, 2 H, G1-*p*-Ar), 6.64 (d, $^4J_{H,H}$ = 2.1 Hz, 4 H, G1-*o*-Ar), 7.26–7.40 (m, 23 H, Ph and pz-H^5 overlapping), 7.62 ppm (d, $J_{H,H}$ = 1.5 Hz, 3 H, pz-H^3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 69.9 (G1-ArCH$_2$O), 70.1 (PhCH$_2$O), 73.4 and 74.0 (-CH$_2$OCH$_2$-), 89.8 [C(pz)$_3$], 101.5 (G0-*p*-Ar and G1-*p*-Ar overlapping), 106.3 (G1-*o*-Ar), 106.4 (G0-*o*-Ar), 106.5 (pz-C^4), 128.0 (*p*-Ph), 127.5 and 128.6 (*o*- and *m*-Ph), 130.9 (pz-C^5), 136.7 (*ipso*-Ph), 139.2 (G1-*ipso*-Ar), 139.5 (G0-*ipso*-Ar), 141.3 (pz-C^3), 159.9 (G0-*m*-Ar), 160.1 ppm (G1-*m*-Ar). IR (KBr pellet): ν 1517 (m, C=N), 1595 and 1451 (vs, C=C), 1296 (s, C–O–C$_{as}$), 1146 and 1037 cm^{-1} (s, C–O–C$_s$). MS (ESI$^+$-TOF in CH$_2$Cl$_2$/MeOH/NH$_4$HCOO 5 mM): *m*/*z* 1804.78 [(M − pz − H)$_2$]$^+$, 1010.22 [M + K]$^+$, 992.40 [M + Na − H]$^+$, 767.30 [M − 3 pz − 2H]$^+$.

(G3-*dend*)OCH$_2$C(pz)$_3$ (4). (G3-*dend*)Br (993 mg, 0.60 mmol) and NaOCH$_2$C(pz)$_3$ (160 mg, 0.60 mmol). The resulting yellow oil was triturated repeatedly with diethyl ether to give a solid. Yield: 895 mg (82%). Anal. Calc. for $C_{116}H_{102}N_6O_{15}$ (1820.12): C, 76.55; H, 5.65; N, 4.62%. Found: C, 76.25; H, 5.59; N, 4.58%. ^{1}H NMR (CDCl$_3$): δ 4.42 (s, 2 H, G0–ArCH$_2$O), 4.88 (s, 4 H, G1–ArCH$_2$O), 4.94 (s, 8 H, G2–ArCH$_2$O), 4.99 (s, 16 H, PhCH$_2$O), 5.09 [s, 2 H, CH$_2$C(pz)$_3$], 6.27 (dd, $J_{H,H}$ = 1.6, 2.5 Hz, 3 H, pz-H^4), 6.41 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H, G0-*o*-Ar), 6.50 (t, $^4J_{H,H}$ = 1.7 Hz, 1 H, G0-*p*-Ar), 6.52 (t, $^4J_{H,H}$ = 2.0 Hz, 2 H, G1-*p*-Ar), 6.54 (t, $^4J_{H,H}$ = 2.2 Hz, 4 H, G2-*p*-Ar), 6.62 (d, $^4J_{H,H}$ = 2.0 Hz, 4 H, G1-*o*-Ar), 6.65 (d, $^4J_{H,H}$ = 2.2 Hz, 8 H, G2-*o*-Ar), 7.26–7.40 (m, 43 H, Ph and pz-H^5 overlapping), 7.62 ppm (d, $J_{H,H}$ = 1.6 Hz, 3 H, pz-H^3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 70.0 (G1-ArCH$_2$O), 70.1 (G2-ArCH$_2$O and PhCH$_2$O overlapping), 73.4 and 73.9 (-CH$_2$OCH$_2$-), 89.8 [C(pz)$_3$], 101.5 (G0-*p*-Ar, G1-*p*-Ar and G2-*p*-Ar overlapping), 106.3 (G1-*o*-Ar, G2-*o*-Ar overlapping), 106.4 (G0-*o*-Ar), 106.5 (pz-C^4), 127.9 (*p*-Ph), 127.5 and 128.5 (*o*- and *m*-Ph), 130.8 (pz-C^5), 136.7 (*ipso*-Ph), 139.1 (G1-*ipso*-Ar and G2-*ipso*-Ar overlapping), 139.5 (G0-*ipso*-Ar), 141.2 (pz-C^3), 159.9 (G0-*m*-Ar), 160.0 (G1-*m*-Ar), 160.1 ppm (G2-*m*-Ar). IR (KBr pellet): ν 1516 (w, C=N), 1595 and 1451 (vs, C=C), 1295 (s, C–O–C$_{as}$), 1155 and 1047 cm^{-1} (vs, C–O–C$_s$). MS (ESI$^+$-TOF in CH$_2$Cl$_2$/MeOH/NH$_4$HCOO 5 mM): *m*/*z* 1842.73 [M + Na]$^+$, 1797.47 [M − pz + HCOO]$^+$, 242.28 [OCH$_2$C(pz)$_3$ − H]$^+$.

General procedure for the preparation of [Mo(CO)$_3${(G*n*-*dend*)-OCH$_2$C(pz)$_3$}] (5–8). Molybdenum compounds **5–8** were prepared by combining the corresponding ligand **1–4** and [Mo(CO)$_3$(η^6-1,3,5-C$_6$H$_3$Me$_3$)] in THF (30 mL) in a Schlenk tube at room temperature and stirring for 4–5 h. The solvent was removed under reduced pressure and the residue washed with pentane or diethyl ether to give **5–8** as yellow solids.

[Mo(CO)$_3${(G0-*dend*)OCH$_2$C(pz)$_3$}] (5). (G0-*dend*)OCH$_2$-C(pz)$_3$ (**1**; 100 mg, 0.30 mmol) and [Mo(CO)$_3$(η^6-1,3,5-C$_6$H$_3$Me$_3$)] (88 mg, 0.29 mmol). Yield: 133 mg (86%). Anal. Calcd. for $C_{21}H_{18}MoN_6O_4$ (514.35): C, 49.04; H, 3.53; N, 16.34%. Found: C, 48.62; H, 3.69; N, 16.53%. ^{1}H NMR ([D$_6$]acetone): δ 5.20 (s, 2 H, PhCH$_2$O), 5.87 [s, 2 H, CH$_2$C(pz)$_3$], 6.47 (dd, $J_{H,H}$ = 1.5, 2.5 Hz, 3 H, pz-H^4), 7.35–7.45 (m, 3 H, Ph), 7.50–7.55 (m, 2 H, Ph), 8.02 (d, $J_{H,H}$ = 2.5 Hz, 3 H, pz-H^5), 8.42 ppm (d, $J_{H,H}$ = 1.5 Hz, 3 H, pz-H^3). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ 68.7 and 74.3 (-CH$_2$OCH$_2$-), 85.2 [C(pz)$_3$], 107.6 (pz-C^4), 129.2, 129.3 and 129.5 (Ph), 133.9 (pz-C^5), 137.0 (*ipso*-Ph), 146.3 (pz-C^3), 229.9 ppm (CO). IR (KBr pellet): ν 1906 and 1795 (vs, CO), 1517 (m, C=N). MS (ESI$^+$-TOF in THF/MeOH/NH$_4$HCOO 5 mM): *m*/*z* 1028.70 [M$_2$]$^+$, 515.36 [M + H]$^+$, 486.34 [M − CO]$^+$, 458.33 [M− 2 CO]$^+$, 430.32 [M − 3 CO]$^+$, 357.37 [**1** + Na]$^+$, 335,39 [**1** + H]$^+$, 199.23 [**1** − 2 pz − H]$^+$.

[Mo(CO)$_3${(G1-*dend*)OCH$_2$C(pz)$_3$}] (6). (G1-*dend*)OCH$_2$-C(pz)$_3$ (**2**; 109 mg, 0.20 mmol) and [Mo(CO)$_3$(η^6-1,3,5-C$_6$H$_3$Me$_3$)] (60 mg, 0.20 mmol). Yield: 123 mg (85%). Anal. Calc. for

$C_{35}H_{30}MoN_6O_6$ (726.60): C, 57.86; H, 4.16; N, 11.57%. Found: C, 57.28; H, 3.96; N, 11.76%. ^{1}H NMR ([D$_6$]acetone): δ 5.10 (s, 6 H, $ArCH_2O$ and $PhCH_2O$ overlapping), 5.82 [s, 2 H, $CH_2C(pz)_3$], 6.45 (m, 3 H, pz-H^4), 6.69 (t, $^4J_{H,H}$ = 2.0 Hz, 1 H, *p*-Ar), 6.78 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H, *o*-Ar), 7.30–7.45 (m, 10 H, Ph), 8.02 (m, 3 H, pz-H^5), 8.38 ppm (m, 3 H, pz-H^3). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ 70.5 ($PhCH_2O$), 68.6 and 74.2 ($-CH_2OCH_2-$), 85.2 [$C(pz)_3$], 102.6 (*p*-Ar), 107.7 (pz-C^4), 108.2 (*o*-Ar), 128.7 (*p*-Ph), 128.4 and 129.3 (*o*- and *m*-Ph), 133.8 (pz-C^5), 138.1 (*ipso*-Ph), 139.1 (*ipso*-Ar), 146.3 (pz-C^3), 161.1 (*m*-Ar), 229.9 ppm (CO). IR (KBr pellet): ν 1900 and 1774 (vs, CO), 1519 (m, C=N), 1598 and 1448 (s, C=C), 1297 (s, C–O–C_{as}), 1160 and 1061 cm^{-1} (s, C–O–C_s). MS (ESI$^+$-TOF in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* 1454.20 [M_2]$^+$, 1189.20 [M_2 − Mo(CO)$_6$]$^+$, 1116.25 [(**2**)$_2$Na]$^+$, 727.61 [M + H]$^+$, 569.23 [**2** + Na]$^+$, 411.18 [**2** − 2 pz − H]$^+$.

[Mo(CO)$_3${(G2-*dend*)$OCH_2C(pz)_3$}] (7). (G2-*dend*)$OCH_2C(pz)_3$ (**3**; 110 mg, 0.11 mmol) and [Mo(CO)$_3$(η^6-1,3,5-$C_6H_3Me_3$)] (32 mg, 0.11 mmol). Yield: 105 mg (83%). Anal. Calc. for $C_{63}H_{54}MoN_6O_{10}$ (1151.10): C, 65.74; H, 4.73; N, 7.30%. Found: C, 65.35; H, 4.64; N, 7.19%. ^{1}H NMR ([D$_6$]acetone): δ 5.06 (s, 4 H, G1-$ArCH_2O$), 5.08 (s, 8 H, $PhCH_2O$), 5.10 (s, 2 H, G0-$ArCH_2O$), 5.80 [s, 2 H, $CH_2C(pz)_3$], 6.42 (m, 3 H, pz-H^4), 6.64 (t, $^4J_{H,H}$ = 2.1 Hz, 2 H, G1-*p*-Ar), 6.68 (t, $^4J_{H,H}$ = 2.1 Hz, 1 H, G0-*p*-Ar), 6.72 (d, $^4J_{H,H}$ = 2.1 Hz, 4 H, G1-*o*-Ar), 6.81 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H, G0-*o*-Ar), 7.26–7.45 (m, 20 H, Ph), 7.98 (m, 3 H, pz-H^5), 8.36 ppm (m, 3 H, pz-H^3). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ 70.3 (G1-$ArCH_2O$), 70.5 ($PhCH_2O$), 68.5 and 74.4 (–CH_2OCH_2–), 85.1 [$C(pz)_3$], 101.9 (G1-*p*-Ar), 102.7 (G0-*p*-Ar), 107.2 (G1-*o*-Ar), 107.6 (pz-C^4), 108.6 (G0-*o*-Ar), 128.6 (*p*-Ph), 128.5 and 129.3 (*o*- and *m*-Ph), 133.8 (pz-C^5), 138.1 (*ipso*-Ph), 139.0 (G0-*ipso*-Ar), 140.5 (G1-*ipso*-Ar), 146.1 (pz-C^3), 161.0 (G1-*m*-Ar), 161.1 (G0-*m*-Ar), 229.9 ppm (CO). IR (KBr pellet): ν 1904 and 1785 (vs, CO), 1517 (m, C=N), 1594 and 1451 (vs, C=C), 1295 (s, C–O–C_{as}), 1155 and 1053 cm^{-1} (s, C–O–C_s). MS (ESI$^+$-TOF in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* 1152.10 [M + H]$^+$, 994.11 [**3** + Na]$^+$, 768.91 [**3**–3 pz − H]$^+$.

[Mo(CO)$_3${(G3-*dend*)$OCH_2C(pz)_3$}] (8). (G2-*dend*)$OCH_2C(pz)_3$ (**4**; 114 mg, 0.06 mmol) and [Mo(CO)$_3$(η^6-1,3,5-$C_6H_3Me_3$)] (18 mg, 0.06 mmol). Yield: 102 mg (85%). Anal. Calc. for $C_{119}H_{102}MoN_6O_{18}$ (2000.09): C, 71.46; H, 5.14; N, 4.20%. Found: C, 71.21; H, 4.93; N, 3.85%. ^{1}H NMR ([D$_6$]acetone): δ 5.00 (s, 8 H, G2-$ArCH_2O$), 5.02 (s, 4 H, G1-$ArCH_2O$), 5.06 (s, 18 H, $PhCH_2O$ and G0-$ArCH_2O$ overlapping), 5.77 [s, 2 H, $CH_2C(pz)_3$], 6.40 (m, 3 H, pz-H^4), 6.61 (m, 7 H, G0-*p*-Ar, G1-*p*-Ar and G2-*p*-Ar overlapping), 6.68 (d, $^4J_{H,H}$ = 2.2 Hz, 4 H, G1-*o*-Ar), 6.71 (d, $^4J_{H,H}$ = 2.2 Hz, 8 H, G2-*o*-Ar), 6.78 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, G0-*o*-Ar), 7.26–7.45 (m, 40 H, Ph), 7.97 (m, 3 H, pz-H^5), 8.32 ppm (m, 3 H, pz-H^3). ^{13}C{^{1}H} NMR ([D$_6$]acetone): δ 70.4 (G1-$ArCH_2O$), 70.5 (G2-$ArCH_2O$ and $PhCH_2O$ overlapping), 68.6 and 74.4 ($-CH_2OCH_2-$), 85.1 [$C(pz)_3$], 102.0 (G2-*p*-Ar and G1-*p*-Ar overlapping), 102.8 (G0-*p*-Ar), 107.3 (G2-*o*-Ar), 107.4 (G1-*o*-Ar), 107.7 (pz-C^4), 108.6 (G0-*o*-Ar), 128.6 (*p*-Ph), 128.5 and 129.3 (*o*- and *m*-Ph), 133.7 (pz-C^5), 138.1 (*ipso*-Ph), 139.0 (G0-*ipso*-Ar), 140.5 (G1-*ipso*-Ar), 140.6 (G2-*ipso*-Ar), 146.3 (pz-C^3), 161.0 (G1-*m*-Ar), 161.1 (G2-*m*-Ar), 161.2 (G0-*m*-Ar), 230.0 ppm (CO). IR (KBr pellet): ν 1905 and 1787 (vs, CO), 1518 (w, C=N), 1595 and 1449 (vs, C=C), 1294 (s, C–O–C_{as}), 1152 and 1051 cm^{-1} (vs, C–O–C_s). MS (ESI$^+$-TOF in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* 2001.10 [M + H]$^+$.

General procedure for the preparation of [$MoCl_2O_2${(G*n*-*dend*)-$CH(3,5\text{-}Me_2pz)_2$}] (9–12). [$MoCl_2O_2$] was weighed into a Schlenk tube in a dry-box and THF (15 mL) added. A THF (15 mL) solution of one equivalent (see below) of the corresponding chelating ligand (G*n*-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (*n* = 0–3) was added, and the resulting yellow solution was stirred for 1 h at room temperature. The solvent was then removed under vacuum and the residue either washed with diethyl ether or recrystallized from a mixture of toluene and hexane to give compounds **9–12** as white or pale-yellow solids.

[$MoCl_2O_2${(G0-*dend*)$CH(3,5\text{-}Me_2pz)_2$}] (9). (G0-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (79 mg, 0.27 mmol) and [$MoCl_2O_2$] (50 mg, 0.25 mmol). Yield: 110 mg (89%). Anal. Calcd for $C_{18}H_{22}Cl_2MoN_4O_2$ (493.24): C, 43.83; H, 4.50; N, 11.36. Found: C, 43.6; H, 4.05; N, 11.55. ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 6H, pz-Me^5), 2.74 (s, 6H, pz-Me^3), 3.63 (d, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 5.98 (s, 2 H, pz-H^4), 6.09 (t, $J_{H,H}$ = 7.5 Hz, 1 H, CH), 6.81–6.84 (m, 2 H, Ph), 7.14–7.22 ppm (m, 3 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.6 (pz-Me^5), 15.6 (pz-Me^3), 43.0 (CH_2), 69.8 (CH), 109.7 (pz-C^4), 128.9 (*p*-Ph), 128.8 and 129.1 (*o*- and *m*-Ph), 134.4 (*ipso*-Ph), 144.2 (pz-C^5), 157.8 ppm (pz-C^3). IR (KBr pellet): ν 1562 (s, C=N), 1620 (w, C=C), 1459 (s, C=C), 950 (s, Mo=O_{as}), 914 cm^{-1} (s, Mo=O_s). MS (ESI$^+$-TOF in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* 611.79 [(L)$_2$Na]$^+$, 317.39 [L + Na]$^+$, 294.40 [L]$^+$, 199.28 [L − Me_2pz]$^+$; L = (G0-*dend*)$CH(3,5\text{-}Me_2pz)_2$.

[$MoCl_2O_2${(G1-*dend*)$CH(3,5\text{-}Me_2pz)_2$}] (10). (G1-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (127 mg, 0.25 mmol) and [$MoCl_2O_2$] (48 mg, 0.24 mmol). Yield: 146 mg (86%). Anal. Calc. for $C_{32}H_{34}Cl_2MoN_4O_4$ (705.49): C, 54.48; H, 4.86; N, 7.94%. Found: C, 54.44; H, 4.71; N, 8.32%. ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 6 H, pz-Me^5), 2.73 (s, 6 H, pz-Me^3), 3.53 (d, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 4.90 (s, 4 H, $PhCH_2O$), 5.97 (s, 2 H, pz-H^4), 6.00 (t, $J_{H,H}$ = 7.5 Hz, 1 H, CH partially overlapped), 6.04 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, *o*-Ar), 6.46 (t, $^4J_{H,H}$ = 2.2 Hz, 1 H, *p*-Ar), 7.30–7.40 ppm (m, 10 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.6 (pz-Me^5), 16.6 (pz-Me^3), 43.0 (CH_2), 69.6 (CH), 69.9 ($PhCH_2O$), 101.7 (*p*-Ar), 107.9 (pz-C^4), 108.0 (*o*-Ar), 127.4 and 128.7 (*o*- and *m*-Ph), 128.1 (*p*-Ph), 136.5 (*ipso*-Ar), 136.6 (*ipso*-Ph), 144.3 (pz-C^5), 157.7 (pz-C^3), 159.9 ppm (*m*-Ar). IR (KBr pellet): ν 1561 (s, C=N), 1595 and 1460 (s, C=C), 1295 (vs, C–O–C_{as}), 1151 and 1030 (s, C–O–C_s), 956 (s, Mo=O_{as}), 920 cm^{-1} (s, Mo=O_s). MS (ESI$^+$-TOF in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* = 1036.29 [(L)$_2$Na]$^+$, 529.64 [L + Na]$^+$, 507.66 [L + H]$^+$, 411.52 [L − Me_2pz]$^+$, 316.40 [L − 2 Me_2pz]$^+$; L = (G1-*dend*)$CH(3,5\text{-}Me_2pz)_2$.

[$MoCl_2O_2${(G2-*dend*)$CH(3,5\text{-}Me_2pz)_2$}] (11). (G2-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (140 mg, 0.15 mmol) and [$MoCl_2O_2$] (30 mg, 0.15 mmol). Yield: 140 mg (87%). Anal. Calc. for $C_{60}H_{58}Cl_2MoN_4O_8$ (1129.99): C, 63.78; H, 5.17; N, 4.96%. Found: C, 63.81; H, 5.46; N, 5.01%. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 6 H, pz-Me^5), 2.71 (s, 6 H, pz-Me^3), 3.52 (d, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 4.84 (s, 4 H, $ArCH_2O$), 5.01 (s, 8 H, $PhCH_2O$), 5.95 (s, 2 H, pz-H^4), 5.98 (t, $J_{H,H}$ = 7.3 Hz, 1 H, CH partially overlapped), 6.01 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, G0-*o*-Ar), 6.48 (t, $^4J_{H,H}$ = 2.2 Hz, 1 H, G0-*p*-Ar), 6.55 (t, $^4J_{H,H}$ = 2.2 Hz, 2 H, G1-*p*-Ar), 6.66 (d, $^4J_{H,H}$ = 2.2 Hz, 4 H, G1-*o*-Ar), 7.30–7.44 ppm (m, 20 H, Ph). ^{1}H NMR

(C_6D_6): δ 1.32 (s, 6 H, pz-Me^5), 2.75 (s, 6 H, pz-Me^3), 3.57 (d, $J_{H,H}$ = 7.5 Hz, 2 H, CH_2), 4.75 (s, 12 H, $ArCH_2O$ and $PhCH_2O$ overlapping), 5.36 (s, 2 H, pz-H^4), 5.65 (t, $J_{H,H}$ = 7.3 Hz, 1 H, CH), 6.13 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H, G0-*o*-Ar), 6.60 (t, $^4J_{H,H}$ = 2.0 Hz, 2 H, G1-*p*-Ar), 6.64 (t, $^4J_{H,H}$ = 2.0 Hz, 1 H, G0-*p*-Ar), 6.69 (d, $^4J_{H,H}$ = 2.2 Hz, 4 H, G1-*o*-Ar), 7.05–7.30 ppm (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 11.0 (pz-Me^5), 16.7 (pz-Me^3), 43.1 (CH_2), 69.8 (CH and $ArCH_2O$ overlapping), 70.1 ($PhCH_2O$), 101.7 (G1-*p*-Ar), 102.3 (G0-*p*-Ar), 106.5 (G1-*o*-Ar), 108.2 (pz-C^4), 109.5 (G0-*o*-Ar), 127.9 and 128.7 (*o*- and *m*-Ph), 128.1 (*p*-Ph), 137.2 (*ipso*-Ph), 137.3 (G0-*ipso*-Ar), 139.8 (G1-*ipso*-Ar), 144.2 (pz-C^5), 157.7 (pz-C^3), 160.6 (G0-*m*-Ar), 160.8 ppm (G1-*m*-Ar). IR (KBr pellet): ν 1562 (s, C=N), 1595 and 1452 (vs, C=C), 1291 (vs, C–O–C_{as}), 1159 and 1046 (vs, C–O–C_s), 959 (s, Mo=O_{as}), 923 cm^{-1} (s, Mo=O_s). MS (ESI$^+$-TOF in toluene/MeOH/NH_4HCOO 5 mM): *m*/*z* 1885.28 $[(L)_2Na]^+$,1169.09 $[M + K]^+$, 1152.98 $[M + Na]^+$, 954.13 $[L + Na]^+$, 932.15 $[L + H]^+$, 836.01 $[L - 2Me_2pz]^+$; L = (G2-*dend*)$CH(3,5\text{-}Me_2pz)_2$.

$[MoCl_2O_2\{$(G3-*dend*)$CH(3,5\text{-}Me_2pz)_2\}]$ (12). (G3-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (150 mg, 0.08 mmol) and $[MoCl_2O_2]$ (16 mg, 0.08 mmol). Yield: 0.122 g (77%). Anal. Calc. for $C_{116}H_{106}Cl_2MoN_4O_{16}$ (1978.98): C, 70.40; H, 5.40; N, 2.83%. Found: C, 69.85; H, 5.62; N, 2.93%. ^1H NMR (C_6D_6): δ 1.34 (s, 6 H, pz-Me^5), 2.75 (s, 6 H, pz-Me^3), 3.53 (d, $J_{H,H}$ = 8.1 Hz, 2 H, CH_2), 4.68 (s, 4 H, G1-$ArCH_2O$), 4.72 (s, 16 H, $PhCH_2O$), 4.76 (s, 8 H, G2-$ArCH_2O$), 5.37 (s, 2 H, pz-H^4), 5.64 (t, $J_{H,H}$ = 8.1 Hz, 1 H, CH), 6.12 (broad d, 2 H, G0-*o*-Ar), 6.64 (broad t, 5 H, G0-*p*-Ar and G2-*p*-Ar overlapping), 6.70 (broad t, 2 H, G1-*p*-Ar), 6.73 (broad d, 4 H, G1-*o*-Ar), 6.76 (broad d, 8 H, G2-*o*-Ar), 7.00–7.30 ppm (m, 40 H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 11.0 (pz-Me^5), 16.8 (pz-Me^3), 43.0 (CH_2), 69.7 (CH), 70.1 (G1-$ArCH_2O$, G2-$ArCH_2O$ and $PhCH_2O$ overlapping), 101.8 (G1-*p*-Ar), 101.9, (G2-*p*-Ar), 102.4 (G0-*p*-Ar), 106.6 (G1-*o*-Ar), 106.7 (G2-*o*-Ar), 108.3 (pz-C^4), 109.6 (G0-*o*-Ar), 127.8 and 128.7 (*o*- and *m*-Ph), 127.9 (*p*-Ph), 137.3 (G0-*ipso*-Ar), 137.4 (*ipso*-Ph), 139.8 (G2-*ipso*-Ar), 139.9 (G1-*ipso*-Ar), 144.4 (pz-C^5), 157.7 (pz-C^3), 160.3 (G0-*m*-Ar), 160.7 (G1-*m*-Ar), 161.1 ppm (G2-*m*-Ar). IR (KBr pellet): ν 1560 (s, C=N), 1598 and 1447 (vs, C=C), 1294 (vs, C–O–C_{as}), 1163 and 1047 (vs, C–O–C_s), 954 (s, Mo=O_{as}), 919 cm^{-1} (s, Mo=O_s). MS (ESI+ in toluene/MeOH/NH_4HCOO 5 mM): *m*/*z* 1803.13 $[L + Na]^+$, 1780.14 $[L + H]^+$; L = (G0-*dend*)$CH(3,5\text{-}Me_2pz)_2$.

General procedure for the preparation of $[Mo(CO)_3L\{$(G*n*-*dend*)-$CH(3,5\text{-}Me_2pz)_2\}]$ [L = CO (13, 14) and NCMe (15)]. The molybdenum precursor ($[Mo(CO)_6]$, $[Mo(CO)_3(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)]$, or $[Mo(CO)_3(NCMe)_3]$) was placed in an ampoule equipped with a PTFE valve together with the appropriate amount of the corresponding ligand (G*n*-dend)$CH(3,5\text{-}Me_2pz)_2$ (*n* = 0, 1, see below) and toluene (20 mL). The tube was sealed and the mixture stirred at room temperature for 4 h (**15**) or warmed at 55 °C for four (**13**) or seven days (**14**), applying vacuum briefly and periodically through the PTFE valve. Compounds **13–15** precipitated out of the reaction mixture as off-white to brown solids, which were filtered and washed with hexane and diethyl ether.

$[Mo(CO)_4\{$(G0-*dend*)$CH(3,5\text{-}Me_2pz)_2\}]$ (13). (G0-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (100 mg, 0.34 mmol) and $[Mo(CO)_6]$ (90 mg, 0.34 mmol). Yield: 130 mg (76%). Anal. Calc. for $C_{22}H_{22}MoN_4O_4$ (502.38): C, 52.60; H, 4.41; N, 11.15%. Found: C, 52.58; H, 3.90; N, 11.27%. ^1H NMR ([D$_6$]acetone): δ 2.16 (s, 6 H, pz-Me^5), 2.55 (s, 6 H, pz-Me^3), 4.11 (d, $J_{H,H}$ = 7.8 Hz, 2 H, CH_2), 6.08 (s, 2 H, pz-H^4), 6.45 (t, $J_{H,H}$ = 7.8 Hz, 1 H, CH), 7.02–7.10 (m, 2 H, Ph), 7.22–7.30 ppm (m, 3 H, Ph). $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ 11.2 (pz-Me^5), 16.7 (pz-Me^3), 40.1 (CH_2), 69.6 (CH), 108.4 (pz-C^4), 128.4 (*p*-Ph), 129.5 and 130.2 (*o*- and *m*-Ph), 135.5 (*ipso*-Ph), 144.3 (pz-C^5), 155.5 (pz-C^3), 206.5 and 208.0 (CO *cis* to pz), 221.1 ppm (CO *trans* to pz). IR (KBr pellet): ν 2012, 1890, 1868 and 1809 (vs, CO), 1565 (s, C=N), 1495 cm^{-1} (s, C=C). MS (ESI+ in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* 894.74 $[(M - 2\ CO + H)_2]^+$, 475.38 $[M–CO + H]^+$, 451.40 $[M - 3\ CO + MeOH + H]^+$, 447.37 $[M - 2\ CO + H]^+$, 419.36 $[M - 3\ CO + H]^+$, 391.34 $[M - 4\ CO + H]^+$, 317.39 $[L + Na]^+$, 199.28 $[L - Me_2pz]^+$; L = (G0-*dend*)-$CH(3,5\text{-}Me_2pz)_2$.

$[Mo(CO)_4\{$(G1-*dend*)$CH(3,5\text{-}Me_2pz)_2\}]$ (14). (G1-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (106 mg, 0.21 mmol) and $[Mo(CO)_6]$ (66 mg, 0.25 mmol). Yield: 115 mg (77%). Anal. Calc. for $C_{36}H_{34}MoN_4O_6$ (714.63): C, 60.51; H, 4.80; N, 7.84%. Found: C, 60.25; H, 4.45; N, 7.32%. ^1H NMR ([D$_6$]acetone): δ 2.13 (s, 6 H, pz-Me^5), 2.56 (s, 6 H, pz-Me^3), 4.00 (d, $J_{H,H}$ = 7.7 Hz, 2 H, CH_2), 5.02 (s, 4 H, $PhCH_2O$), 6.11 (s, 2 H, pz-H^4), 6.30 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, *o*-Ar), 6.37 (t, $J_{H,H}$ = 7.5 Hz, 1 H, CH), 6.56 (t, $^4J_{H,H}$ = 2.2 Hz, 1 H, *p*-Ar), 7.30–7.50 ppm (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ 11.4 (pz-Me^5), 16.8 (pz-Me^3), 40.3 (CH_2), 69.4 (CH), 70.3 ($PhCH_2O$), 102.7 (*p*-Ar), 108.6 (pz-C^4), 109.1 (*o*-Ar), 128.3 and 129.3 (*o*- and *m*-Ph), 128.7 (*p*-Ph), 137.6 (*ipso*-Ph), 138.1 (*ipso*-Ar), 144.6 (pz-C^5), 155.6 (pz-C^3), 161.1 (*m*-Ar), 206.4 and 207.9 (CO *cis* to pz), 221.8 ppm (CO *trans* to pz). IR (KBr pellet): ν 2012, 1883, 1869 and 1832 (vs, CO), 1562 (s, C=N), 1593 and 1459 (s, C=C), 1290 (s, C–O–C_{as}), 1150 and 1029 cm^{-1} (s, C–O–C_s). MS (ESI+ in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* 1036.28 $[(L)_2Na]^+$, 687.63 $[M–CO + H]^+$, 529.64 $[L + Na]^+$, 507.27 $[L + H]^+$, 411.52 $[L - Me_2pz]^+$; L = (G1-*dend*)$CH(3,5\text{-}Me_2pz)_2$.

$[Mo(CO)_3(NCMe)\{$(G0-*dend*)$CH(3,5\text{-}Me_2pz)_2\}]$ (15). (G0-*dend*)$CH(3,5\text{-}Me_2pz)_2$ (85 mg, 0.29 mmol) and $[Mo(CO)_3(NCMe)_3]$ (88 mg, 0.29 mmol). Yield: 120 mg (80%). Anal. Calc. for $C_{23}H_{25}MoN_5O_3$ (515.42): C, 53.60; H, 4.89; N, 13.59%. Found: C, 53.82; H, 4.85; N, 13.69%. ^1H NMR ([D$_6$]acetone): δ 2.05 (s, 3 H, CH_3CN), 2.15 (s, 6H, pz-Me^5), 2.43 (s, 6H, pz-Me^3), 4.38 (d, $J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 5.96 (s, 2 H, pz-H^4), 6.45 (t, $J_{H,H}$ = 8.0 Hz, 1 H, CH), 7.15–7.20 (m, 2 H, Ph), 7.22–7.30 ppm (m, 3 H, Ph). $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ 11.2 (pz-Me^5), 16.1 (pz-Me^3), 40.0 (CH_2), 69.8 (CH), 107.8 (pz-C^4), 128.1 (*p*-Ph), 129.3 and 130.6 (*o*- and *m*-Ph), 136.4 (*ipso*-Ph), 142.7 (pz-C^5), 154.2 (pz-C^3), 206.7 (CO *cis* to pz), 227.6 ppm (CO *trans* to pz). IR (KBr pellet): ν = 1906 and 1764 (vs, CO), 1562 (s, C=N), 1494 cm^{-1} (s, C=C). MS (ESI$^+$-TOF in THF/MeOH/NH_4HCOO 5 mM): *m*/*z* 611.79 $[(L)_2Na]^+$, 519.46 $[M–CO + MeOH]^+$, 475.38 $[M–MeCN + H]^+$, 451.40 $[M - 2\ CO–MeCN + MeOH + H]^+$, 317.39 L + Na]$^+$, 199.28 $[L - Me_2pz]^+$; L = (G0-*dend*)$CH(3,5\text{-}Me_2pz)_2$.

Spectroscopic characterization of $[MoClO_2\{$G*n*-(*dend*)$OCH_2C(pz)_3\}]Cl$

G0. ^1H NMR ($CDCl_3$): δ 4.26 (s, 2 H, $PhCH_2O$), 4.67 [s, 2 H, $CH_2C(pz)_3$], 6.55 (dd, $J_{H,H}$ = 1.5, 2.8 Hz, 2 H, pz-H^4), 6.63 (dd, $J_{H,H}$ = 1.5, 2.8 Hz, 1 H, pz-H^4), 6.86 (d, $J_{H,H}$ = 2.8 Hz, 2 H, pz-H^5), 7.10–7.15 (m, 2 H, Ph), 7.25–7.30 (m, 3 H, Ph), 7.94 (d,

$J_{H,H}$ = 1.5 Hz, 1 H, pz-H^3), 7.99 (d, $J_{H,H}$ = 2.8 Hz, 1 H, pz-H^5), 8.93 ppm (d, $J_{H,H}$ = 1.5 Hz, 2 H, pz-H^3).

G1. ^{1}H NMR ($CDCl_3$): δ 4.16 (s, 2 H, $ArCH_2O$), 4.62 [s, 2 H, $CH_2C(pz)_3$], 4.98 (s, 4 H, $PhCH_2O$), 6.37 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, *o*-Ar), 6.55 (m, 3 H, pz-H^4 and *p*-Ar overlapping), 6.63 (dd, $J_{H,H}$ = 1.8, 2.6 Hz, 1 H, pz-H^4), 6.81 (d, $J_{H,H}$ = 2.6 Hz, 2 H, pz-H^5), 7.30–7.38 (m, 10 H, Ph), 7.95 (2 broad d, 1 + 1 H, pz-H^3 and pz-H^5, overlapping), 8.91 ppm (d, $J_{H,H}$ = 1.8 Hz, 2 H, pz-H^3).

G2. ^{1}H NMR ($CDCl_3$): δ 4.17 (s, 2 H, G0-$ArCH_2O$), 4.64 [s, 2 H, $CH_2C(pz)_3$], 4.94 (s, 4 H, G1-$ArCH_2O$), 5.03 (s, 8 H, $PhCH_2O$), 6.37 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H, G0-*o*-Ar), 6.50 (t, $^4J_{H,H}$ = 2.3 Hz, 2 H, G1-*p*-Ar), 6.57 (m, 3 H, pz-H^4 and G0-*p*-Ar, overlapping), 6.62 (m, 1 H, pz-H^4), 6.65 (d, $^4J_{H,H}$ = 2.3 Hz, 4 H, G1-*o*-Ar), 6.82 (d, $J_{H,H}$ = 2.4 Hz, 2 H, pz-H^5), 7.30–7.40 (m, 20 H, Ph), 7.92 (d, $J_{H,H}$ = 1.5 Hz, 1 H, pz-H^3), 7.95 (d, $J_{H,H}$ = 2.4 Hz, 1 H pz-H^5), 8.91 ppm (d, $J_{H,H}$ = 1.5 Hz, 2 H, pz-H^3).

G3. ^{1}H NMR ($CDCl_3$): δ 4.13 (s, 2 H, G0-$ArCH_2O$), 4.59 [s, 2 H, $CH_2C(pz)_3$], 4.91 (s, 4 H, G1-$ArCH_2O$), 4.94 (s, 8 H, G2-$ArCH_2O$), 5.00 (s, 16 H, $PhCH_2O$), 6.36 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H, G0-*o*-Ar), 6.44 (t, $^4J_{H,H}$ = 2.2 Hz, 2 H, G1-*p*-Ar), 6.52 (t, $^4J_{H,H}$ = 2.2 Hz, 4 H, G2-*p*-Ar), 6.55 (m, 3 H, pz-H^4 and G0-*p*-Ar, overlapping), 6.61 (d, $^4J_{H,H}$ = 2.2 Hz, 4 H, G1-*o*-Ar), 6.62 (m, 1 H, pz-H^4), 6.65 (d, $^4J_{H,H}$ = 2.2 Hz, 8 H, G2-*o*-Ar), 6.78 (d, $J_{H,H}$ = 2.4 Hz, 2 H, pz-H^5), 7.25–7.40 (m, 40 H, Ph), 7.86 (d, $J_{H,H}$ = 1.5 Hz, 1 H, pz-H^3), 7.91 (broad d, 1 H, pz-H^5), 8.86 ppm (d, $J_{H,H}$ = 1.5 Hz, 2 H, pz-H^3).

DOSY experiments

The diffusion coefficients were measured at 25 °C by using the Dbppste (DOSY Bipolar Pulse Simulated Echo) pulse sequence in a Varian NMR System 500 equipped with a high accuracy variable temperature unit (± 0.1 °C), a Performa IV PFG amplifier, and a Z-PFG Triple Resonance 5-mm probe. Fine calibration of the PFG strength (DAC to G unit) was performed with an H_2O/HDO (2 Hz) sample as standard supplied by Varian (D = 19.04 × 10^{-10} m^2 s^{-1} at 25 °C). The diffusion NMR data (Fig. 4) were acquired over 64 scans, with settings pw90, an acquisition time of 3 s, a relaxation delay of 2 s, in each one of the 15 steps of the gradient level array between 1 and 50 G cm^{-1} (50 ms of diffusion delay and 2 ms of total defocusing time). The experimental data (32 K × 1 K) was treated with the "DOSY" software from VNMRJ2.1B.

X-Ray crystallographic studies

Single crystals of **13** and **15** suitable for X-ray diffraction studies were obtained from their corresponding reaction mixtures in C_6D_6 in NMR tubes. A summary of the crystal data, data collection, and refinement parameters for the structural analysis of each compound is given in Table 2. Suitable crystals were covered with mineral oil and mounted in the N_2 stream of a Bruker-Nonius Kappa-CCD diffractometer equipped with an area detector and an Oxford Cryostream 700 unit; data were collected using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 200 K, with an exposure time of 10 s per frame (5 sets; 266 frames; phi and omega scan 2° scan-width) for compound

Table 2 Crystal data and structure refinement for compounds **13** and **15**

	13	**15·C_6H_6**
Empirical formula	$C_{22}H_{22}MoN_4O_4$	$C_{29}H_{31}MoN_5O_3$
Formula weight	502.938	593.537
Color	Yellow	Yellow
Temperature/K	200.0(2)	200.0(2) K
Wavelength (λ)/Å	0.71069	0.71069 Å
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, P-1
Unit cell dimensions:		
a/Å	12.651(5)	12.280(5)
b/Å	12.999(5)	12.284(5)
c/Å	13.437(5)	19.122(5)
α/°		83.470(5)
β/°	96.271(5)	89.970(5)
γ/°		89.760(5)
Volume/Å^3	2196.5(1.5)	2865.8(1.8)
Z, Calculated density/g cm^{-3}	4, 1.519	4, 1.376
Absorption coefficient/mm^{-1}	0.633	0.495
F(000)	1024	1224
Crystal size/mm	0.40 × 0.40 × 0.3	0.50 × 0.23 × 0.23
θ ranges/°	3.05 to 27.51	3.05 to 27.50
Limiting indices	$-16 \le h \le 16$, $-16 \le k \le 16$, $-17 \le l \le 17$	$-15 \le h \le 15$, $-15 \le k \le 15$, $-24 \le l \le 23$
Reflections collected/unique	42259/5053 [R_{int} = 0.1094]	25236/13133 [R_{int} = 0.13120]
Reflections observed	4008 [$I > 2\sigma(I)$]	5790 [$I > 2\sigma(I)$]
Completeness to θ (%)	99.8	99.8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5053/0/368	13133/0/707
Goodness of fit on F^2	1.131	1.035
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0358, wR_2 = 0.0814	R_1 = 0.0755, wR_2 = 0.1729

[a] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR_2 = \{[\Sigma \omega (F_o^2 - F_c^2)] / [\Sigma \omega (F_o^2)^2]\}^{1/2}$.

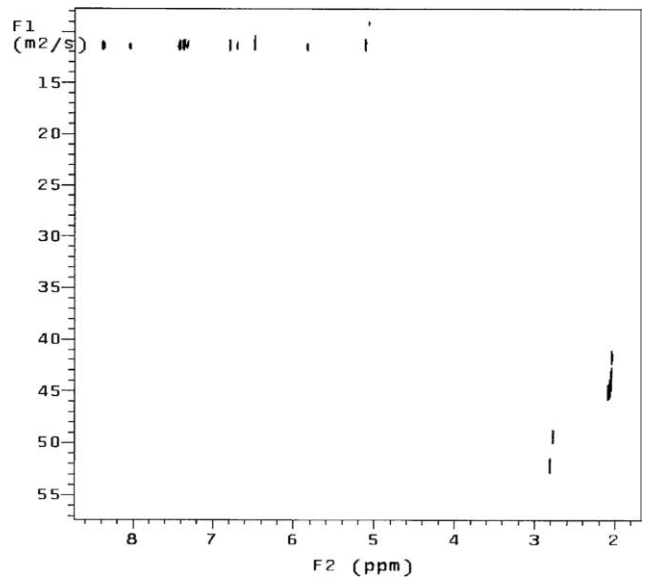


Fig. 4 2D diffusion spectrum for compound **6**.

13, and an exposure time of 36 s per frame (11 sets; 526 frames; phi and omega scans 1.8° scan-width) for compound **15**. Raw data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares on F^2 with SHELXL-97.[40] Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. Most of the hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX program.[41] Space group $P2_1/c$ was also tested for **15** but neither refinement nor resolution was satisfactory.

CCDC reference numbers 652159 & 652160.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710125b

Catalytic procedure using compounds 9–12

The corresponding catalyst precursor was weighed (3.7 μmol, adjusted for catalytic Mo concentration of 0.05 mol%) into a 20-mL screw-capped Schlenk tube containing a magnetic stirrer. The vial was capped and sealed with a septum, purged by repeated argon/vacuum operations, and thermostatted at 55 °C. *n*-Dibutyl ether (800 mg as internal standard) and *cis*-cyclooctene (800 mg, 7.3 mmol) were then added with a syringe and the reaction was started by adding *tert*-butyl hydroperoxide (2 mL, 5.5 M in n-decane) with vigorous stirring. Stirring of the mixture was maintained and samples were withdrawn periodically, treated to remove hydroperoxide and water,[26] and analyzed by GC.

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