New manganese-scaffolded organic triple-deckers based on quinoxaline, pyrazine and pyrimidine cores†

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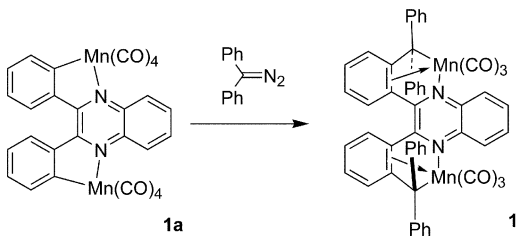
The thermolytic coupling of Ph_2CN_2 and (*t*-Bu)(Ph)CN_2 with doubly cyclomanganated 2,5-diphenylpyrazine and 4,6-diphenylpyrimidine afforded substantial amounts of new triple decker compounds of either C_i and C_2 symmetry respectively containing, in both series, two η^3-bonded $Mn(CO)_3$ fragments which intervene as scaffolds sustaining the helical non-conjugated triaryl backbone. The molecular structures of two pyrazine derivatives show a typical non-parallel stacking of the aromatic rings and the encapsulation of the central pyrazyl fragment with interplanar centroid-to-centroid distances of *ca.* 3.5 Å. The stacking of the aromatics in the triple-decker pyrimidine derivatives has been assessed by ^{1}H NMR experiments at low temperature. All the triple-decker-type compounds are electroactive. Pyrimidine triple-deckers can reversibly be electrochemically reduced to the corresponding anions.

Introduction

It is well established that diaza-heterocycles, also known as "diazines", display a reasonable electron affinity, which stems from their low lying vacant π-orbitals.[1] This intrinsic property is the base for the elaboration of electron transporting polymers[2] intended to be used in organic semi-conducting devices. Even though diazines can readily be converted to their parent radical-anion, upon thorough chemical or electrochemical reductions in aprotic solvents with more than one electron per molecule the corresponding anions often collapse by intra- or inter-molecular carbon–carbon coupling reactions.[3] Diazines are convenient electron transfer mediators or radical traps,[4] photo-initiators in radical polymerization,[5] and can be readily reduced by various means and converted to their hydro analogs.[6] π-Radical anions of diazines tend to form charged diaromatic clusters with their neutral parent.[7]

Even though coordination of the heterocyclic nitrogen atoms to transition metals may result in an increase of the cathodic reduction potentials and stable ligand-centered radical anions,[8] highly reduced species are generally unstable and subject to ECE processes that lead to de-coordination or ligand alteration.[9] This drawback should *a priori* disqualify electro-generated diazine π-radicals as efficient spin-carriers. A reasonable solution could reside in the elaboration of an "electron nest-type" architecture in which the spin density generated at an aromatic diazine core would be protected from external chemical interactions by encapsulation within a rigid and relatively electrochemically inert structure.

In a previous report[10] it was shown that such an architecture could readily be built by the thermolytic coupling of a pro-helical bis-cyclomanganated quinoxaline derivative **1a** with Ph_2CN_2 (eqn (1)) leading to a stable C_2 symmetric triple decker architecture **1b** encapsulating a quinoxalyl core. The propensity of the latter to sustain reduction by two successive reversible mono-electron processes leading to the formation of the corresponding radical-anion and the dianion has been established.[11] Herein, we disclose some results on the reactivity of various bis-cyclomanganated quinoxaline, pyrazine and pyrimidine derivatives towards 1-phenyldiazomethanes, the syntheses of new examples of metallo-organic triple-decker molecular systems containing pyrazyl or pyrimidyl heterocyclic cores and a preliminary study of their electrochemical properties in reductive conditions.



1a **1b** (1)

Results and discussion

Bis-cyclomanganated quinoxaline, pyrazine and pyrimidine derivatives, *viz.* **1a–4a** and **6a** (*vide infra*) were investigated for their ability to undergo coupling reactions with aryldiazomethanes with the aim of synthesizing new triple-decker systems with different heterocyclic cores. In all cases the coupling reactions were carried out in boiling solvents with a sufficient excess of diazoalkane in order to compensate its decomposition, which takes place unavoidably at high temperatures. Two aryldiazomethanes were used in this study; 1,1-diphenyldiazomethane and 1-*tert*-butyl-1-phenyldiazomethane.

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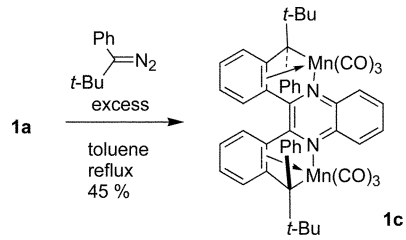
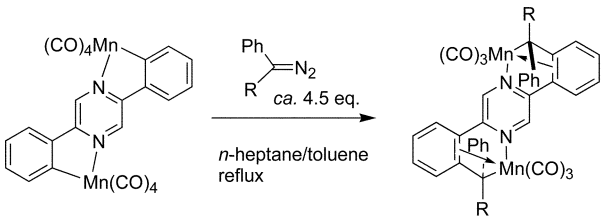


(2)

Triple deckers

We first set out to check the degree of stereoselectivity attainable by coupling a non symmetric diazoalkane such as (*t*-Bu)(Ph)CN_2 using **1a** as a model substrate. Indeed, the insertion of the prochiral diazoalkane (*t*-Bu)(Ph)CN_2 into the two C-Mn bonds of the substrate should give rise to two stereogenic centres, allowing in principle the formation of three stereo-isomers containing either the two *t*-Bu groups in an *endo*:*endo*, *exo*:*endo* or/and in an *exo*:*exo* position. The treatment of **1a** with an excess of (*t*-Bu)(Ph)CN_2 in refluxing toluene afforded a single product **1c** in 45% yield after chromatographic purification (eqn (2)), of which the structure corresponds to the *exo*-*exo* *t*-Bu stereochemistry proposal. This blue-colored compound was crystallized and analyzed by X-ray diffraction analysis. Fig. 1 displays an ORTEP diagram of **1c**, which shows clearly that the double *anti* insertion of the carbene moiety (*t*-Bu)(Ph)C: is controlled by steric factors that favor the orientation of the less sterically encumbering substituent, *e.g.* the phenyl group, in the *endo* position, leading to a triple-decker arrangement akin to that noticed with **1b**.[11]



(3)

Pyrazine derivative **2a** reacted cleanly with excesses of both Ph_2CN_2 and (*t*-Bu)(Ph)CN_2 in boiling mixtures of *n*-heptane and toluene affording the corresponding products **2b** and **2c**, respectively, in 67 and 61% yield (eqn (3)). The stereochemistry of complex **2c** and particularly the positions of the phenyl and *tert*-butyl groups were assessed by X-ray diffraction analysis. An ORTEP diagram of the structure of compound **2c** is displayed in Fig. 2. Again in this case the (*t*-Bu)(Ph)C moiety inserts in a stereoselective way to yield a triple-decker arrangement.

Due to the presence of a disordered molecule of toluene surrounded with unassigned residual electron density in the unit cell of **2b**, the refinement of the structure could not be optimized. However, partial X-ray data confirmed the structural similarity of **2b** with **2c** (*cf.* the CIF provided).

The reaction of **3a**[12] with Ph_2CN_2 in a boiling mixture of *n*-heptane and toluene afforded compound **3b** in 84% yield after chromatographic purification (Scheme 1). In contrast, the reaction of **3a** with (*t*-Bu)(Ph)CN_2 proved to be sluggish and afforded a mixture of three complexes (Scheme 1), which were separated by flash chromatography at low temperature: traces of the double-decker

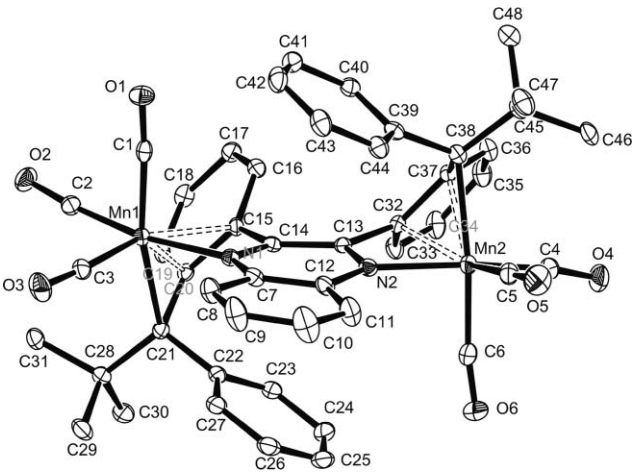


Fig. 1 ORTEP diagram of compound **1c** drawn at 30% probability level. Hydrogen atoms and solvation molecule have been omitted for the sake of clarity. Selected interatomic distances (Å) and angles (°): Mn(1)–N(1) 2.042(2), Mn(1)–C(21) 2.208(3), Mn(1)–C(20) 2.219(3), Mn(1)–C(15) 2.283(3); C(21)–Mn–C(3) 94.4(1). Distance (Å) between centroids (C(22)–C(27))–(quinoxalyl): 3.396(6). Torsion angle (°): C(13)–C(14)–C(15)–C(16) 47.2, C(14)–C(13)–C(32)–C(33) 46.1. Interplanar angle (°): (phenyl)–(quinoxalyl): 28.

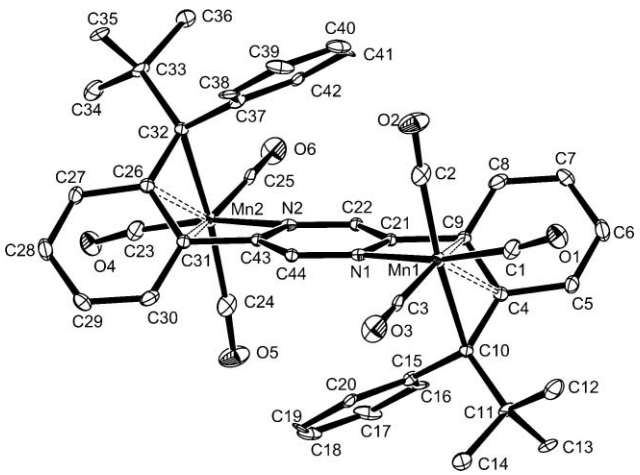
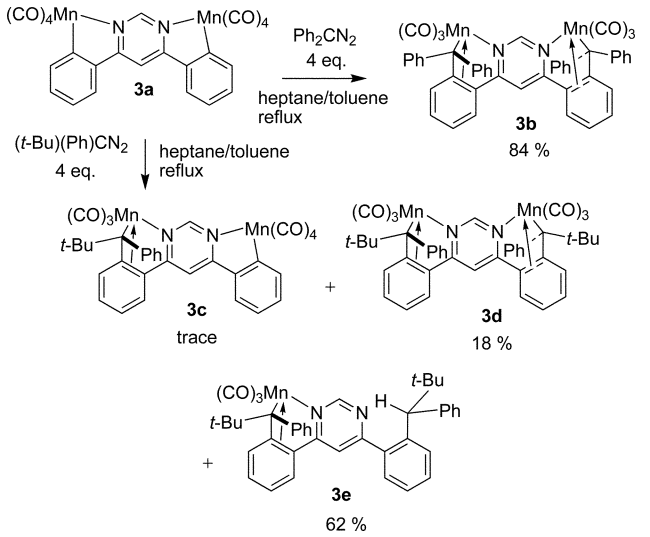


Fig. 2 ORTEP diagram of compound **2c** drawn at 30% probability level. Hydrogen atoms and solvation molecule have been omitted for the sake of clarity. Selected inter-atomic distances (Å) and angles (°): Mn(1)–N(1) 2.045(8), Mn(1)–C(10) 2.197(9), Mn(1)–C(4) 2.23(1), Mn(1)–C(9) 2.363(9); C(10)–Mn–C(3) 95.2(4). Distance (Å) between centroids (C(15)–C(20))–(pyrazyl): 3.445(9). Torsion angles (°): N(1)–C(21)–C(9)–C(4) 54.1, C(21)–C(9)–C(4)–C(10) 9.8, C(9)–C(4)–C(10)–C(15) 49.2, C(4)–C(10)–C(15)–C(16) 40.9. Interplanar angle (°): (phenyl)–(pyrazyl): 32.

complex **3c**, of which the structure was confirmed by ^{1}H NMR and X-ray diffraction (Fig. 3), triple-decker complex **3d** in 18% yield and complex **3e** in 62% yield. The latter seemingly results from a homolytic hydrogenative mono-demetallation of **3d**. An ORTEP diagram representing the molecular structure of **3e** is displayed in Fig. 4. The triple-decker arrangement of the phenyl and pyrimidyl rings in **3b** and **3d** could not be confirmed by X-ray diffraction analysis due to repeated failure in obtaining suitable crystals.

However, ^{1}H NMR spectroscopy at sub-ambient temperature provided some clear evidence that the phenyl groups were proximal



Scheme 1

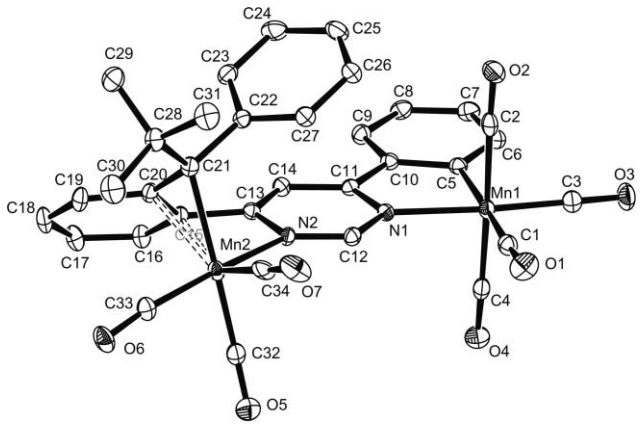


Fig. 3 ORTEP diagram of compound **3c** drawn at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Mn(1)–C(3) 1.799(3), Mn(1)–C(4) 1.851(3), Mn(1)–N(1) 2.070(2), Mn(1)–C(5) 2.047(3), Mn(1)–C(1) 1.826(3), Mn(1)–C(2) 1.858(3),
Mn(2)–N(2) 2.035(4), Mn(2)–C(15) 2.415(4), Mn(2)–C(20) 2.234(4), Mn(2)–C(21) 2.206(4). Distance (Å) between centroids: (pyrimidyl)–(C(22)–C(27)): 3.341(4). Torsion angles (°): C(16)–C(15)–C(13)–C(14) 40.5, N(2)–C(13)–C(15)–C(20) 52.0, C(15)–C(20)–C(21)–C(22) 46.1, C(20)–C(21)–C(22)–C(23) 39.2.

(*endo*) to the central pyrimidyl moiety. Indeed, like reported previously for **1b**,[11] *endo* phenyl groups in both **3b** and **3d** sustain a strong hindrance to rotation because of their vicinity to the diazinyl moiety. In the ^{1}H NMR spectrum (500 MHz, 223 K) of **1c**, for example, the five protons of the *endo*-phenyl groups appeared as separate signals at δ 5.92 (t*), 6.56 (t*), 6.61 (d) 6.73 (d) and 6.92 (t*) ppm. With **3d**, at 223 K in deuterated chloroform, all five protons of the *endo*-phenyl group were located as five separate and well resolved signals at δ 6.18 (d), 6.82 (t*), 7.00 (d), 7.05 (t*), 7.15 (t*) ppm. A two-dimensional ^{1}H–^{1}H ROESY experiment carried out at 223 K (500 MHz) indicated that the triplet of the *endo*-phenyl group at δ 6.82 ppm and the doublet of the same group at 7.00 ppm correlate "through space" with the two protons of the pyrimidine group, which show up as singlets at δ 4.60 and 7.37 ppm, respectively (*cf*. ESI†). These two signals are assigned to

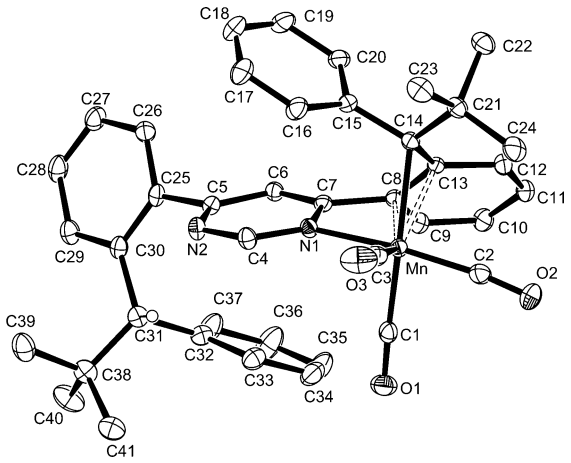
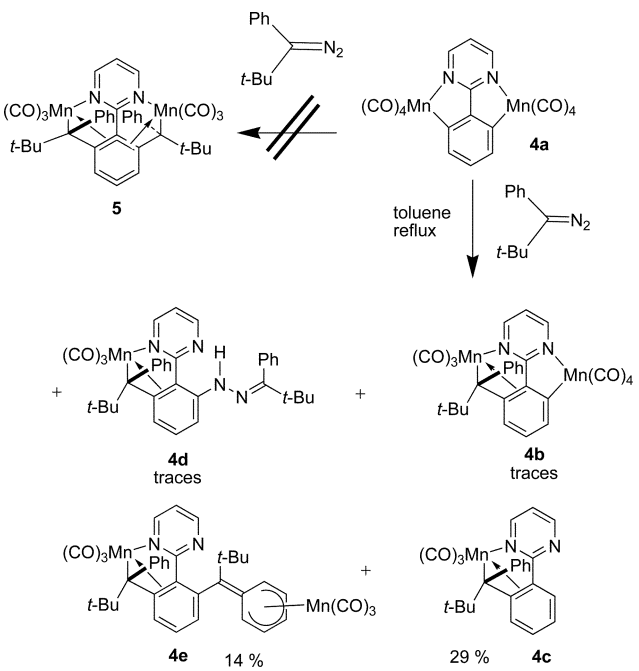


Fig. 4 ORTEP diagram of compound **3e** drawn at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Mn–N(1) 2.021(2), Mn–C(8) 2.344(5), Mn–C(13) 2.196(2), Mn–C(14) 2.217(2). Distance (Å) between centroids: (pyrimidyl)–(C(15)–C(20)): 3.482(5). Torsion angles (°): C(26)–C(25)–C(5)–C(6) 62.5, N(1)–C(7)–C(8)–C(13) 52.6, C(8)–C(13)–C(14)–C(15) 47.0.

the protons occupying the 5 and the 2 positions at the heterocycle, respectively.

We set out to probe the reactivity of complex **4a** towards both Ph_2CN_2 and (*t*-Bu)(Ph)CN_2 having in sight the possible formation of a triple-decker such as **5** in which we expected the *anti*-facial double coordination of the central phenyl group by two manganese centers sharing the same π-electrons (Scheme 2). Whereas several attempts to react **4a** with Ph_2CN_2 resulted essentially in the decomposition of the reagents into intractable material, an experiment carried out with (*t*-Bu)(Ph)CN_2 resulted in the formation of four different products in low yields, **4b–e**, among which the latter, **4e**, clearly results from the incorporation of two (*t*-Bu)(Ph)C: moieties into **4a** upon decarbonylation. Compound



Scheme 2

4e, isolated after chromatographic separation in 14% yield, is an interesting case of homodinuclear species containing two $Mn(CO)_3$ moieties bonded to the organic backbone following two different hapto modes: a η^2–η^1 benzyl and η^5-benzylidene mode. Fig. 5 displays an ORTEP diagram of the latter's structure. The C(29)–C(28) bond distance of 1.353(3) Å is similar to those reported for exocyclic double bonds in analogous complexes.[13]

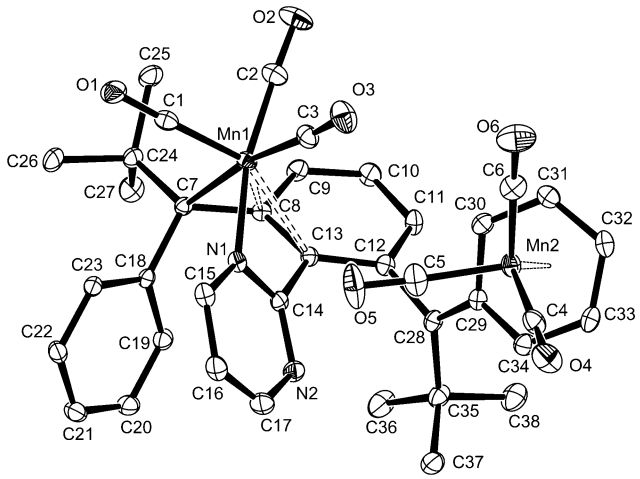
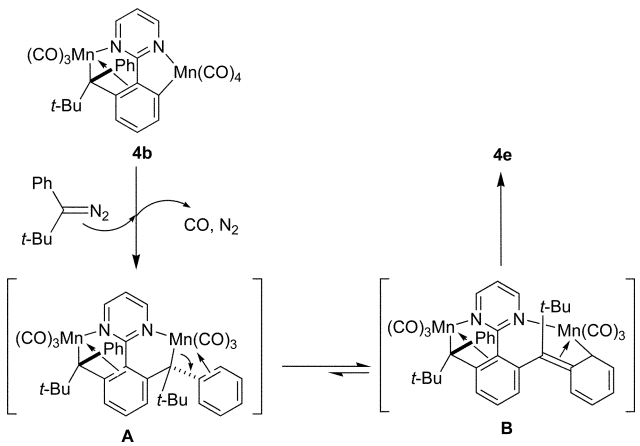


Fig. 5 ORTEP diagram of compound **4e** drawn at 30% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Mn(1)–N(1) 2.012(2), Mn(1)–C(14) 2.649(4), Mn(1)–C(13) 2.409(4), Mn(1)–C(8) 2.210(2), Mn(1)–C(7) 2.219(2), Mn(2)–C(30) 2.253(3), Mn(2)–C(31) 2.143(3), Mn(2)–C(32) 2.118(3), Mn(2)–C(33) 2.143(2), Mn(2)–C(34) 2.258(3), Mn(2)–C(29) 2.706(4), C(8)–C(9) 1.440(3), C(9)–C(10) 1.356(4), C(10)–C(11), 1.402(4), C(11)–C(12) 1.372(3), C(12)–C(13) 1.444(3), C(13)–C(8) 1.459(3), C(28)–C(29) 1.353(3), C(28)–C(12) 1.503(3). Selected interatomic angles (°): C(29)–C(28)–C(12) 118.4(2), C(29)–C(28)–C(35) 124.0(2), C(12)–C(28)–C(35) 116.5(2).

Worthy to note here, the distance from atom O(5) to the centroid of the pyrimidyl ring (C(14),N(2),C(17),C(16),C(15),N(1)) amounts only *ca.* 2.55 Å, suggesting a stabilizing carbonyl–π interaction. The process leading to the formation of **4e** necessarily involves the haptotropic migration of one $Mn(CO)_3$ moiety accompanied with a cleavage of the N–Mn bond as proposed in Scheme 3.



Scheme 3

In the initial stage of the reaction, (*t*-Bu)(Ph)CN_2 reacts with **4a** to give a first η^1:η^2-benzylic double-decker intermediate **4b**, which undergoes a second insertion of a (*t*-Bu)(Ph)C: alkylidene to yield successively transients A and B. It is likely that the latter evolves to give **4e** rather than **5** because the π-system of the central phenyl group, which is already involved in a bonding interaction with one $Mn(CO)_3$ fragment, cannot accommodate a second electron-demanding $Mn(CO)_3$ group. Compound **4c**, which was recovered in 29% yield, seemingly results from a hydrogenative mono-demetallation of **4b**. Compounds **4d** and **4b** were recovered in yields lower than 5% and could only be subjected to limited analytical characterization.

The structure of **4d** was nonetheless established by X-ray diffraction analysis (Fig. 6). The presence of the hydrazyl moiety suggests that **4d** results from a coupling reaction of **4b** with the residual amounts of hydrazone (*t*-Bu)(Ph)C=N–NH_2 present in the sample of (*t*-Bu)(Ph)CN_2 used in the experiment.

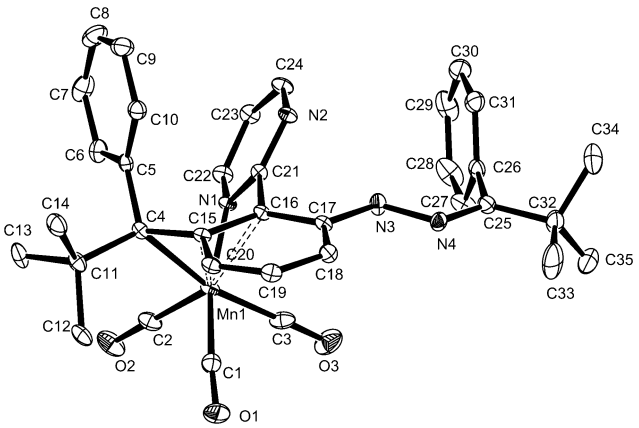
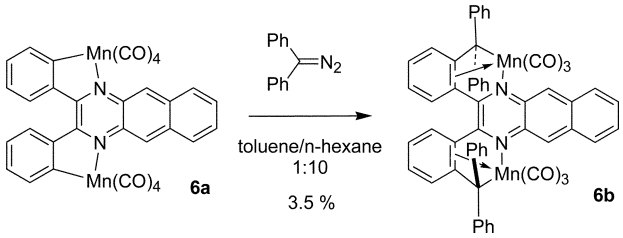


Fig. 6 ORTEP diagram of compound **4d** drawn at 30% probability level. Hydrogen atoms and solvents have been omitted for clarity. Selected interatomic distances (Å): Mn–N(1) 2.019(4), Mn–C(16) 2.279(5), Mn–C(15) 2.227(5), Mn–C(4) 2.228(5), C(15)–C(16) 1.472(7), C(16)–C(17) 1.432(7), C(17)–C(18) 1.377(7), C(18)–C(19) 1.399(8), C(19)–C(20) 1.358(8), C(20)–C(15) 1.429(7), N(3)–N(4) 1.381(6), N(3)–C(17) 1.383(7), N(4)–C(25) 1.283(7). Selected interatomic angles (°): C(25)–N(4)–N(3) 116.3(4), N(4)–N(3)–C(17) 119.5(4).

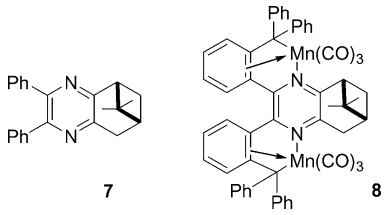
Finally, repeated attempts to react either Ph_2CN_2 or (*t*-Bu)(Ph)CN_2 with **6a**[14] in boiling *n*-hexane were not granted with success, the experiments producing a large amount of untractable decomposition material. Upon thorough chromatographic treatment however, a limited amount of compound **6b** could be recovered (eqn (4)). From the spectroscopic point of view, this benzo-analog of compound **1b** presents ^1H and ^{13}C NMR features that support a triple decker molecular arrangement. If one compares the IR spectra of **1c** and **1b**[11] to that of **6b**, it appears that the C–O stretching bands generated by the $Mn(CO)_3$ scaffold of the latter appear at frequencies about 7–10 cm^{-1} higher. This is a direct consequence of the extension of the π-heterocyclic system from quinoxalyl to benzo[*g*]quinoxalyl, which induces a higher π-accepting ability of the coordinated diazine and reduces the back-donation of electron density from the Mn centre to the π* orbitals of the carbonyls.

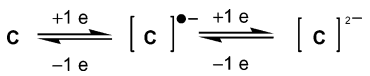


(4)

Electrochemical properties of the new triple-deckers

The electrochemical behaviour of **1c**, **2b**, **2c**, **3b**, **3d** and **6b** was investigated by cyclic voltammetry at room temperature. Under cathodic reduction conditions, **1c**, **3b** and **3d** displayed two reversible waves corresponding to the successive formation of the radical-anions and dianions (Scheme 4), at moderately negative potentials, well above those measured in similar conditions for the bare metal-free heterocycles (Table 1), *e.g.* 2,3-diphenylquinoxaline (−1.63 V *vs.* SCE in CH_3CN)[15] and 4,6-diphenylpyrimidine (−1.88 V *vs.* SCE in CH_3CN). Further reduction of **3b** and **3d** at lower potentials revealed a third reversible process, which was not assigned. At a scan rate of 200 mV s^{-1} compounds **2b–c** displayed a series of three-to-four close reduction waves at potentials slightly higher than for 2,5-diphenylpyrazine (−1.85 V *vs.* SCE in CH_3CN) with reverse oxidation waves symptomatic of a possible fast chemical degradation of the reduced species through a ECE scheme. Interestingly another pyrazine-based triple-decker terpenic derivative **8**[16] displayed two relatively distant reversible reduction waves, the first one occurring at a potential more positive by 0.8 V than that measured for the metal-free parent pyrazine ligand **7** (−2.24 V, $\Delta E_{c/a} = 186$ mV, scan rate 800 mV s^{-1}, MeCN). A comparison of the reduction potentials of **1b**[11] and **6b**, although measured in different conditions, gives a good illustration of how the extension of the π-aromatic system at the central heterocycle lowers the energy of the LUMOs, which are populated upon reduction. The two reversible reduction processes measured for **6b** occur at potentials about 0.4 V higher than for **1b**.





Scheme 4

Preliminary spectroscopic characterizations of radical anion 3b

Negative mode electrospray mass spectroscopy measurements carried out with a fresh solution containing $[\mathbf{3b}]^{\bullet-}$ afforded a composite spectrum containing a large signal corresponding to $[\mathbf{3b} - H]^-$ and other peaks of higher m/z ratio seemingly resulting from various products of reaction with the solvent, namely 1,2-dimethoxyethane (Fig. 7). In the conditions used for the generation of the radical anion $[\mathbf{3b}]^{\bullet-}$, *e.g.* by reaction of a solution of **3b** with a potassium mirror, it can be speculated that reactive dianionic species may coexist in solution and therefore be responsible for the formation of products of higher molecular weight either before or during the formation of the sprayed droplets of solution in the spectrometer's injection chamber. Interestingly, $[\mathbf{1b}]^-$, which was prepared by the same procedure was analyzed by electrospray mass spectrometry upon direct injection, producing a clean spectrum containing exclusively the molecular parent peak with an isotopic pattern matching ideally the theory (*cf.* ESI†).

Conclusion

In summary, we have demonstrated that the thermolytic coupling of two phenyldiazomethanes with two examples of doubly metallated pyrazine and pyrimidine derivatives could afford substantial amounts of new triple-decker compounds of either C_2 (**3b** and **3d**) or C_i (**2b** and **2c**) symmetry. In all these cases the stereochemical course of the double insertion of the alkylidene moiety obeyed the "*anti* pathway" already observed in the formation of **1b**[11] and **1c** (this work). With other bis-cyclomanganated diazines, *i.e.* **4a** and **6a**, the coupling reaction with diazoalkanes was quite sluggish and led to complex mixtures or decomposition. As observed with **1b** in a previous report,[11] the reduction potentials of the isolated triple-decker systems are more positive than for the parent metal free ligands putatively as a consequence of the coordination of the central heterocycle to the relatively electron-withdrawing $Mn(CO)_3$ moieties. Unfortunately, the complex electrochemical behaviour of **2b–c** suggests that reductive conditions possibly induce structural changes and a loss of the triple-decker architecture. The electro-spray MS investigation of reduced **3b** has casted some doubt on the chemical inertness of the corresponding anions. Thorough EPR spectroscopic investigations coupled with

Table 1 Reduction potentials measured at room temperature with 10^{-4} M solutions in the presence of ferrocene as the internal reference. Potentials were extrapolated against the standard calomel electrode

	1c	2b	2c	3b	3d	6b	8
Solvent[e]	MeCN	THF	THF	MeCN	MeCN	DMF	MeCN
Scan rate[a]	400	50	50	200	200	80	100
$E_{1/2}$[c] ($\Delta E_{c/a}$)[d]	−1.02 (71)	−1.42 (113)	−1.22 (95)	−1.24 (42)	−1.36 (87)	−0.59 (104)	−1.41 (76)
	−1.80 (183)[b]	−1.60 (104)[b]	−1.48 (95)[b]	−1.52 (86)	−1.57 (115)	−1.44 (80)	−1.77 (70)
		−2.04 (119)[b]	−1.72 (115)[b]	−1.91 (248)[b]	−1.97 (247)[b]		
			−2.09 (180)[b]				

[a] In mV s^{-1}. [b] Delayed reverse oxidation due uncompensated resistance. [c] In V. [d] $|E_c - E_a|$ in mV. [e] Abbreviations: DMF dimethylformamide, THF tetrahydrofurane, MeCN acetonitrile.

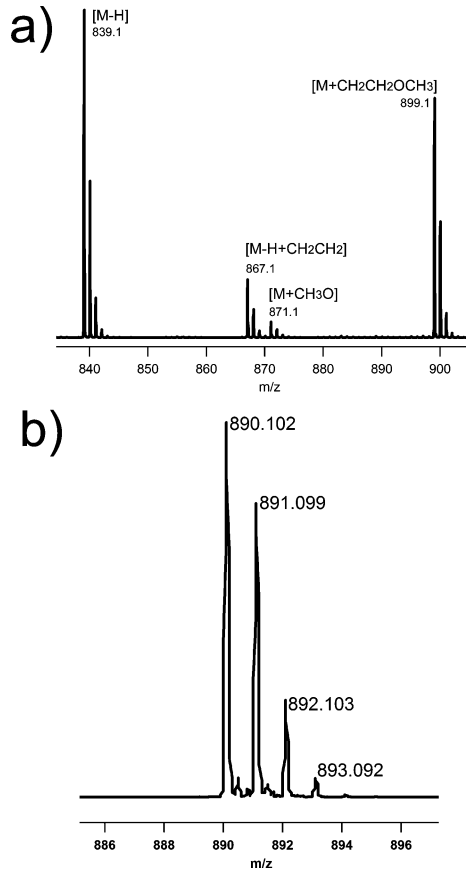


Fig. 7 Negative mode electro-spray mass spectra obtained upon direct injection of samples of **3b** (a) and **1b** (b) upon preliminary reduction over a potassium mirror in 1,2-dimethoxyethane at room temperature.

the theoretical determination of the electronic structure of the radical anions are underway in order to evaluate the extent and the consequences of the possible geometrical distortions of the triple-decker architectures. Our current efforts are also focussing on evaluating the most reliable and suitable manganese-scaffolded triple-decker systems for a use as electron hosts in spin carriers.

Experimental

All experiments were carried out under a dry atmosphere of argon with dry and degassed solvents. NMR spectra were acquired on Bruker DRX 500, AV 400 (^{13}C and ^{1}H nuclei) and AV 300 (^{1}H nucleus) spectrometers at room temperature unless otherwise stated. Chemical shifts are reported in parts per million downfield of Me_4Si and coupling constant are expressed in Hz. IR spectra were measured with a Perkin-Elmer FT spectrometer. Mass spectra were recorded at the Service of Mass Spectrometry of University Louis Pasteur (FAB^+ and ES) and at the Analytical Center of the Chemical Institute of the University of Bonn (EI). Electrospray MS measurements were carried out in the negative polarity mode with a MicroTOF Bruker spectrometer. Elemental analyses (reported in mass%) were performed at the Service d'Analyses of the "Institut de Chimie de Strasbourg" and at the analytical center of the "Institut Charles Sadron" in Strasbourg. 2,5-Diphenylpyrazine,[17] **3a**, **4a**, **6a**, 1,1-diphenyldiazomethane[18] and 1-phenyl-1-*tert*-butyldiazomethane[19] were synthesized according to published procedures. Chromatographic separations were performed at sub-ambient temperatures with a Merck Geduran silica (Si 60, 40–60 μm) in columns packed in *n*-hexane or *n*-pentane with a maximum positive argon pressure of 0.5 bar. In special cases, separations required the use of deactivated silica prepared by suspending 200 g of SiO_2 in a mixture of distilled acetone and water (4 wt%); the resulting silica gel was washed with 200 mL of *n*-hexane and briefly dried under reduced pressure prior to use.

Procedure for X-ray diffraction analyses and structure resolution

Acquisition and processing parameters are displayed in Table 2. Reflections were collected with a Nonius KappaCCD diffractometer using Mo-Kα graphite-monochromated radiation (λ = 0.71073 Å). The structures were solved using direct methods and were refined against $|F|$ and for all pertaining computations, the Nonius OpenMoleN package was used.[20] Hydrogen atoms were introduced as fixed contributors.

CCDC reference numbers 284341–284346.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513322j

Electrochemical measurements

All measurements were made at room temperature, under an atmosphere of dry argon with a Princeton Applied Research 273 (Model 270/250) potentiostat computer-controlled with the EGCS Research Electrochemistry software v. 4.23. Tetra-*n*-butylammonium hexafluorophosphate was used as the electrolyte in solution in dry solvents saturated with argon (0.1 M, CH_3CN, DMF, DME, THF) and was generally dried under vacuum two days at 70 °C before use. Cyclic voltammetry experiments were carried out using an undivided cell comprising a three electrode system: a Pt-bead or carbon-paste work electrode (2 mm diameter), a Pt wire of 1 mm diameter as the counter electrode and, due to the sensitivity of the reduced species to water, a silver wire of 1 mm diameter as the pseudo-reference electrode. All potentials were referenced against the ferrocenium–ferrocene (Fc^+/Fc) couple and subsequently extrapolated against standard saturated calomel electrode (SCE).

Syntheses

General procedure for the synthesis of bis-cyclomanganated arenes. The ligand and $PhCH_2Mn(CO)_5$ were dissolved in a mixture of *n*-heptane and toluene and the resulting solution was heated to reflux under a gentle stream of argon during 8 h. The solvents were evaporated, the resulting residue was dissolved in dichloromethane and SiO_2 was added. The suspension was stripped of solvent under reduced pressure and the coated silica gel was loaded on the top of a refrigerated SiO_2 column packed in *n*-hexane or *n*-pentane.

[2,5-(Diphenyl-κ$C^{2'}$,κ$C^{2''}$)]pyrazine-(κN^1,κN^2)bis(tetracarbonylmanganese(I)), 2a. 2,5-Diphenylpyrazine (0.5 g, 2.2 mmol) was mixed with $PhCH_2Mn(CO)_5$ (1.85 g, 6.5 mmol), *n*-heptane (10 mL) and toluene (10 mL) were added and the resulting mixture was refluxed for 9 h. Silica gel was added to the resulting solution and the suspension was stripped of solvent. Flash chromatography (6 °C) on silica gel using a mixture of dichloromethane and

Table 2 List of X-ray diffraction acquisition and refinement data for **1c**, **2c**, **3c**, **3e**, **4e** and **4d**

Compound[a]	**1c**	**2c**	**3c**	**2e**	**4d**	**4e**
Formula	$C_{48}H_{40}Mn_2N_2O_6{\cdot}C_7H_8$	$C_{44}H_{38}Mn_2N_2O_6{\cdot}CH_2Cl_2$	$C_{34}H_{24}Mn_2N_2O_7$	$C_{41}H_{39}MnN_2O_3$	$C_{70}H_{70}Mn_2N_8O_6{\cdot}CH_3OH{\cdot}CH_2Cl_2$	$C_{38}H_{34}Mn_2N_2O_6$
M_r	942.88	885.61	682.46	662.72	1346.24	724.58
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	10.4636(1)	18.8855(3)	16.7067(3)	12.5455(3)	12.0775(2)	9.5308(2)
b/Å	28.2835(3)	13.7903(4)	11.9869(2)	16.0358(4)	11.8548(2)	12.9309(3)
c/Å	15.5722(2)	15.9732(5)	16.2192(3)	17.4291(5)	26.0230(5)	15.1767(6)
α/°						70.543(5)
β/°	100.253(5)	101.257(5)	112.429(5)	95.923(5)	97.232(5)	80.913(5)
γ/°						69.573(5)
V/Å^3	4534.96(11)	4080.0(2)	3002.38(14)	3487.6(2)	3696.2(1)	1650.86(8)
Z	4	4	4	4	2	2
Color	Blue	Dark red	Red	Orange	Orange	Orange
Crystal dim./mm	0.10 × 0.08 × 0.08	0.10 × 0.08 × 0.06	0.22 × 0.20 × 0.18	0.12 × 0.10 × 0.08	0.20 × 0.06 × 0.06	0.12 × 0.10 × 0.06
D_c/g cm^{-3}	1.38	1.44	1.51	1.26	1.21	1.46
F_{000}	1960	1824	1392	1392	1408	748
μ/mm^{-1}	0.612	0.801	0.894	0.419	0.468	0.816
hkl Limits	0,14/0,38/−21,20	−22,22/−17,19/−26,26	−22,22/−16,14/−23,23	0,17/0,21/−23,23	−16,16/−13,16/−36,36	−13,13/−18,12/−21,19
θ Limits/°	2.5/29.13	2.5/29.97	2.5/30.06	2.5/29.09	2.5/30.02	2.5/30.02
No. of data meas.	12451	20231	16229	9646	18493	12849
No. of data with $I > 3\sigma(I)$	6562	3693	4068	5225	4648	5753
No. of variables	586	514	406	424	423	433
R	0.040	0.087	0.033	0.043	0.061	0.038
R_w	0.058	0.099	0.041	0.064	0.087	0.055
GOF	1.052	1.590	1.034	1.149	1.090	1.011
Largest peak in final diff./e Å^{-3}	0.448	0.925	0.262	0.304	1.138	0.502

[a] All analyses were carried out with a Nonius Kappa CCD diffractometer using a Mo-Kα graphite-monochromated source at 173 K.

n-hexane (8 : 2) released a large fraction containing the product. The latter was obtained in analytical pure form as an orange solid (0.84 g, 1.8 mmol, 83% yield). **2a**: Anal. Calc. for $C_{24}H_{10}N_2O_8Mn_2$: C 51.09, H 1.79, N 4.96. Found: C 50.97, H 1.70, N 4.94%. IR (CH_2Cl_2) ν(CO)/cm^{-1}: 2076 (s), 2001 (vs), 1985 (vs), 1944 (s). δ_H ($CDCl_3$) 9.19 (s, 2H), 8.01 (d, 2H, ^3J = 7.2), 7.85 (d, 2H, ^3J = 7.8), 7.36 (t, 2H, ^3J = 7.3), 7.27 (t, 2H, ^3J = 7.3). δ_C ($CDCl_3$) 219.5 (CO), 213.5 (CO), 212.4 (2 CO), 176.6, 158.3, 143.6, 142.5, 142.2, 131.5, 124.8, 124.4.

{2,3-Di[1′2′7′:η-2′-(phenyl(*tert*-butyl)methylene)phenyl]quinoxaline-κ*N*^{1},κ*N*^{2}}bis(tricarbonylmanganese(I)) 1c. Compound **1a** (0.16 g, 0.29 mmol) was dissolved in toluene (15 ml) and the solution brought to reflux. A solution of 1-phenyl-1′-*tert*-butyldiazomethane (0.8 g, 4.6 mmol) in toluene (3 ml) was added dropwise over 45 min. and the resulting mixture was left to boil for an additional 45 min. Silica gel was added to the resulting solution and the suspension was stripped of solvent. Chromatography (5 °C) over silica gel using a mixture of *n*-hexane and dichloromethane (6:4) allowed the elution of a fraction, which afforded a deep purple solid upon removal of the solvents under reduced pressure. The latter was recrystallized from a mixture of dichloromethane and *n*-hexane (0.11 g, 45% yield). Anal. Calc. for $C_{48}H_{40}N_2O_6Mn_2$: C 67.77, H 4.74, N 3.29. Found: C 67.87, H 4.90, N 3.16%. IR (CH_2Cl_2) ν(CO)/cm^{-1}: 1995 (vs), 1925 (s), 1903 (s). δ_H ($CDCl_3$, 223 K) 7.93 (d, 2H, ^3J = 9.2, $H_{Ph\ coordinated}$), 7.78 (m, 2H, $H_{Quinoxaline}$), 7.67 (m, 2H, $H_{Quinoxaline}$), 7.50 (t, 2H, ^3J = 7.4, $H_{Ph\ coordinated}$), 7.00 (t, 2H, ^3J = 7.6, $H_{Ph\ coordinated}$), 6.95 (t, 2H, ^3J = 7.0, H_{Ph}), 6.77 (d, 2H, ^3J = 7.7, $H_{Ph\ coordinated}$), 6.73 (d, 2H, ^3J = 8.0, ^3J = 7.4, H_{Ph}), 6.62 (d, 2H, ^3J = 7.6, H_{Ph}), 6.57 (t, 2H, ^3J = 7.3, H_{Ph}), 1.31 (s, 18H). δ_C ($CDCl_3$) 230.4, 222.5, 219.5, 146.5, 143.0, 140.3, 137.7, 133.8, 132.8, 132.6, 131.8, 131.6, 126.6, 126.4, 124.8, 124.5, 123.6, 117.4, 83.1, 81.2, 39.2 (3 C), 30.8.

{2,5-Di[1′2′7′:η-2′-(diphenylmethylene)phenyl]pyrazine-κ*N*^{1},κ*N*^{2}}-bis(tricarbonylmanganese(I)) 2b. Compound **2a** (0.18 g, 0.38 mmol) was dissolved in a mixture of heptane (10 mL) and toluene (5 mL) and the resulting mixture brought to reflux. A solution of 1,1′-diphenyldiazomethane (0.35 g, 1.8 mmol) in 3 ml toluene was added over 20 min. The resulting mixture was allowed to boil for additional 1 h. Silica gel was added to the resulting solution and the suspension was stripped of solvent. Chromatography (5 °C) on silica gel using a mixture of dichloromethane and *n*-hexane (8 : 2) allowed the elution of a red-coloured fraction. The latter afforded a red solid upon removal of the solvents under reduced pressure, which was recrystallized from a mixture of dichloromethane and *n*-hexane (0.215 g, 67% yield). HRMS (FAB$^+$) Calc. for $C_{45}H_{30}N_2O_3Mn_2$ (M − 3CO): 756.101736. Found 756.101736. IR (CH_2Cl_2) ν(CO)/cm^{-1}: 2002 (vs), 1931 (m), 1912 (m). δ_H ($CDCl_3$) 7.77 (m, 2H), 7.59 (d, 1H, ^3J = 7.9), 7.39 (m, 4H), 7.27 (m, 1H), 7.21 (m, 2H), 7.08 (m, 1H), 6.98 (t, 1H, ^3J = 7.2), 6.87 (t, 1H, ^3J = 7.6), 6.81 (s, 1H), 6.13 (d, 1H, ^3J = 7.3). δ_C ($CDCl_3$) 230.2, 220.4, 220.1, 153.0, 146.9, 146.5, 141.0, 136.3, 134.3 (2 C), 133.1, 131.8, 130.4, 130.2, 129.3, 128.8 (2 C), 128.4, 128.0, 127.9, 126.6, 126.1, 125.2, 113.6, 95.7, 75.9. MS (FAB$^+$): *m*/*z* 841 [M]$^+$, 756 [M − 3CO]$^+$, 672 [M − 6CO]$^+$, 618 [M − 6CO − Mn]$^+$, 563 [M − 6CO − 2Mn]$^+$, 485 [M − 6CO − 2Mn − C_6H_5]$^+$.

{2,5-Di[1′2′7′:η-2′-(phenyl(*tert*-butyl)methylene)phenyl]pyrazine-κ*N*^{1},κ*N*^{2}}bis(tricarbonylmanganese(I)), 2c. Compound **2a** (0.2 g, 0.4 mmol) was dissolved in *n*-heptane (10 ml) and the resulting solution brought to reflux. A solution of 1-phenyl-1′-*tert*-butyldiazomethane (0.32 g, 1.9 mmol) in 3 ml toluene was added over 20 min and the resulting mixture allowed to boil for additional 20 min. Silica gel was added to the resulting solution and the suspension was stripped of solvent. Chromatography (5 °C) over silica gel using a mixture of dichloromethane and *n*-hexane (7 : 3) allowed the elution of a deep red fraction. The latter was stripped of solvents to afford a red-coloured solid (0.21 g, 61% yield). Anal. Calc. for $C_{44}H_{38}N_2O_6Mn_2 \cdot 1/3CH_2Cl_2$: C 64.16, H 4.67, N 3.37. Found: C 64.03, H 4.90, N 3.34%. IR (CH_2Cl_2) ν(CO)/cm^{-1}: 1997 (vs), 1923 (m), 1908 (m). δ_H ($CDCl_3$, 223 K) 7.98 (d, 2H, ^3J = 8.9, $H_{Ph\ coordinated}$), 7.60 (t, 2H, ^3J = 7.8, $H_{Ph\ coordinated}$), 7.35 (t, 2H, ^3J = 7.4, $H_{Ph\ coordinated}$), 7.23 (d, 2H, ^3J = 8.0, $H_{Ph\ coordinated}$), 7.20 (d, 2H, ^3J = 7.9, H_{Ph}), 7.14 (t, 2H, ^3J = 7.6, H_{Ph}), 7.05 (t, 2H, ^3J = 7.4, H_{Ph}), 6.79 (t, 2H, ^3J = 7.5, H_{Ph}), 6.47 (s, 2H, $H_{pyrazine}$), 6.20 (d, 2H, ^3J = 7.7, H_{Ph}), 1.26 (s, 18H). δ_C ($CDCl_3$, 263 K) 229.7, 221.9, 219.4, 153.2, 143.0, 140.4, 138.6, 133.9, 133.6, 132.8, 131.8, 126.9, 126.8, 125.8, 125.1, 116.4, 88.9, 80.9, 39.4 (3 C), 29.9.

{4,6-Di[1′2′7′:η-2′-(diphenylmethylene)phenyl]pyrimidine-κ*N*^{1},κ*N*^{2}}bis(tricarbonylmanganese(I)), 3b. Compound **3a** (0.23 g, 0.4 mmol) was dissolved in a mixture of heptane (10 mL) and toluene (5 mL) and the resulting solution brought to reflux. A solution of 1,1′-diphenyldiazomethane (0.32 g, 1.64 mmol) in 3 ml toluene was added over 20 min. and the resulting mixture was left to boil for additional 40 min. Silica gel was added to the resulting solution and the suspension was stripped of solvent. Chromatography (5 °C) over silica gel using a mixture of dichloromethane and *n*-hexane (7 : 3) allowed the elution of a deep red-coloured fraction containing the product, which was recovered a solid upon removal of the solvents under reduced pressure. The latter was recrystallized from a mixture of dichloromethane and *n*-hexane (0.292 g, 84% yield). Anal. Calc. for $C_{48}H_{30}N_2O_6Mn_2$: C 66.82, H 3.56, N 3.22. Found: C 66.93, H 3.49, N 3.24%. IR (CH_2Cl_2) ν(CO): 2004 (vs), 1929 (m), 1912 (m) cm^{-1}. δ_H (d_6.acetone) 7.75 (s, 1H), 7.72 (m, 4H), 7.63 (m, 2H), 7.60 (m, 4H), 7.45 (d, 2H, ^3J = 8.1), 7.39 (t, 4H, ^3J = 7.7), 7.25 (m, 3H), 7.10 (t, 2H, ^3J = 7.5), 6.91 (m, 6H), 6.40 (d, 2H, ^3J = 7.3). δ_C (d_6-acetone) 231.0, 221.3, 219.4, 167.8, 160.8, 147.9, 147.5, 136.5, 134.5, 133.5, 132.1, 131.2, 129.7, 129.0, 128.6, 128.3, 126.7, 126.4, 116.4, 113.4, 101.6, 77.0.

{4,6-Di[1′2′7′:η-2′-(phenyl(*tert*-butyl)methylene)phenyl]pyrimidine-κ*N*^{1},κ*N*^{2}}bis(tricarbonylmanganese(I)) 3d and {4-[1′2′7′:η-2′-(phenyl(*tert*-butyl)methylene)phenyl]-6-[2′-1″-(phenyl(*tert*-butyl)-methylene)phenyl]pyrimidine-κ*N*^{1}}(tricarbonylmanganese(I)) 3e. Compound **3a** (0.2 g, 0.35 mmol) was dissolved in a mixture of heptane (10 mL) and toluene (5 mL) and the resulting solution brought to reflux. A solution of 1-phenyl-1′-*tert*-butyldiazomethane (0.25 g, 1.45 mmol) in 3 ml toluene was added over 30 min and the resulting mixture was left to boil for an additional 30 min. Silica gel was added to the resulting solution and the suspension was stripped of solvent. Chromatography (5 °C) over deactivated silica using a mixture of *n*-hexane and dichloromethane (8 : 2) allowed the elution of a red–orange fraction containing trace amounts of **3c** (less than 5 mg) and a

red fraction (F1); elution with *n*-hexane and dichloromethane (7 : 3) delivered an orange fraction (F2). Following the same procedure, (F1) was purified by a second flash chromatography with a 9 : 1 mixture of *n*-hexane and dichloromethane (0.5 l) to afford a red band (F1′) and with a 1 : 1 mixture of *n*-hexane and dichloromethane to afford an orange band (F2′). Fractions (F1) and (F1′) were combined to afford upon removal of solvents **3d** as a red solid (0.05 g, 18% yield). Fractions (F2) and (F2′) were combined to afford upon removal of solvents **3e** as an orange solid (0.14 g, 62% yield). **3d**: HRMS (FAB$^+$) Calc. for $C_{41}H_{38}N_2O_3Mn_2$ (M$^+$): 716.164333. Found: 716.164336. Anal. Calc. for $C_{44}H_{38}N_2O_6Mn_2$: C 66.01, H 4.78, N 3.50. Found: C 65.47, H 4.92, N 3.48%. IR (CH_2Cl_2) ν_{CO}/cm^{-1} 2002 (vs), 1915 (s), 1909 (s). δ_H (500 MHz, $CDCl_3$, 223 K) 7.97 (d, 2H, ^3J = 9.0, $H_{Ph\ coordinated}$), 7.54 (t, 2H, ^3J = 7.8, $H_{Ph\ coordinated}$), 7.37 (s, 1H, $H_{pyrimidine}$), 7.21 (t, 2H, ^3J = 7.5, $H_{Ph\ coordinated}$), 7.15 (t, 2H, ^3J = 7.3, H_{Ph}) 7.05 (t, 2H, ^3J = 7.3, H_{Ph}), 7.01 (d, 2H, ^3J = 7.7, H_{Ph}), 6.82 (t*, 2H, H_{Ph}), 6.79 (d, 2H, ^3J = 8.7, $H_{Ph\ coordinated}$), 6.18 (d, 2H, ^3J = 7.5, H_{Ph}), 4.60 (s, 1H, $H_{pyrimidine}$), 1.44 (s, 18H, *t*-Bu). δ_H (300 MHz, C_6D_6, 298 K) 7.85 (d, 2H, ^3J = 9.1), 7.13 (m, 5H), 6.98 (m, 4H), 6.81 (t*, 2H, ^3J = 7.5), 6.64 (d, 2H, ^3J = 8.3), 6.46 (t, 2H, ^3J = 7.4), 5.95 (d, 2H, ^3J = 7.6), 3.90 (s, 1H), 1.5 (s, 18H). δ_C (125 MHz, $CDCl_3$, 263 K) 229.8, 221.7, 220.2, 168.4, 158.6, 144.4, 139.1, 135.6, 133.8, 133.0, 131.3, 128.4, 125.8, 125.4 (2 C), 116.4, 114.8, 91.3, 82.4, 39.3 (3 C), 28.1. MS (FAB$^+$) *m*/*z* 716 (M − 3CO), 661 (M − 3CO − Mn). **3e**: HRMS (FAB$^+$) Calc. for $C_{41}H_{40}N_2O_3Mn$ (M$^+$): 663.241927. Found: 663.241940. Anal. Calc. for $C_{41}H_{39}N_2O_3Mn$: C 74.31, H 5.93, N 4.23. Found: C 74.10, H 6.10, N 4.21%. IR (*n*-hexane) ν(CO): 2002 (vs), 1922 (s), 1915 (s) cm^{-1}. δ_H ($CDCl_3$, 298 K) 8.38 (s, 1H, Ha), 8.06 (d, 1H, ^3J = 9.1, $H_{Ph\ coordinated}$), 7.91 (d, 1H, ^3J = 8.0, H_{Phenyl}), 7.56 (t, 1H, ^3J = 7.9, $H_{Ph\ coordinated}$), 7.41 (t, 1H, ^3J = 7.7, H_{Phenyl}), 7.28 (d*, 1H, H_{Ph1}), 7.20 (m, 5H, $3H_{Ph2}$ (t*) + $1H_{Ph\ coordinated}$ (t*) + $1H_{Phenyl}$ (t*)), 7.03 (d, 1H, ^3J = 8.1, $H_{Ph\ coordinated}$), 6.91 (t, 1H, ^3J = 7.6, H_{Ph1}), 6.82 (m, 3H, $1H_{Ph1}$ (t*, ^3J = 7.1) + $2H_{Ph2}$ (d*, ^3J = 6.1)), 6.63 (d, 1H, ^3J = 7.6, H_{Phenyl}), 6.61 (t, 1H, ^3J = 6.1, H_{Ph1}), 6.16 (d, 1H, ^3J = 7.4, H_{Ph1}), 5.42 (s, 1H, Hb), 3.87 (s, 1H, Hc), 1.46 (s large, 9H, *t*-$Bu_{(a)}$), 1.00 (s, 9H, *t*-$Bu_{(b)}$). δ_C ($CDCl_3$, 298 K) 230.4, 222.0, 221.9, 168.8, 167.4, 158.9, 144.9, 141.0, 140.0, 139.4, 134.6, 134.4, 134.0, 131.0, 130.5 (2 C), 129.1, 128.9, 128.5, 127.8 (2 C), 126.5, 126.1, 126.0 (2 C), 125.0, 124.9, 117.3, 116.4, 90.7, 82.4, 56.8, 39.2, 34.9, 32.7, 29.5 (3 C), 29.1, 27.0 (3 C). MS (FAB$^+$): *m*/*z* 663 [M]$^+$, 578 [M − 3CO]$^+$, 523 [M − 3CO − Mn]$^+$.

(2-{[1′,2′,7′:η-2′-(Phenyl(*tert*-butyl)methylene|(phenyl-κC$^{3'}$)}-pyrimidine-κ*N*^{1})tricarbonylmanganese(I)-κ*N*^{2})tetracarbonylmanganese(I) 4e, {2-[1′,2′,7′:η-2′-(phenyl(*tert*-butyl)methylenephenyl]-pyrimidine-κ*N*^{1}}tricarbonylmanganese(I) 4c, {2-[1′,2′,7′:η-2′-(phenyl(*tert*-butyl)methylene-3′-(*tert*-butyl){tricarbonyl(η^5-phenyl)-manganese(I)}methylene)]pyrimidine-κ*N*^{1}}tricarbonylmanganese(I) 4b and {2-[1′,2′,7′:η-2′-(phenyl(*tert*-butyl)methylene-3′-(2,2-dimethyl-1-phenylpropylidene)hydrazone]phenylpyrimidine-κ*N*^{1}}-tricarbonylmanganese(I) 4d. Compound **4a** (0.204 g, 0.42 mmol) was dissolved in 10 mL toluene and the resulting mixture brought to reflux. A solution of 1-phenyl-1′-*tert*-butyldiazomethane (0.285 g, 1.6 mmol) in 3 mL toluene was added over 25 min, and the resulting solution was left to boil for 25 min. Silica gel was added to the resulting solution and the suspension was stripped of solvent. Chromatography over deactivated silica gel/*n*-hexane (4 °C) with a 9 : 1 mixture of *n*-hexane and dichloromethane, allowed the elution of a red fraction containing **4b** (0.045 g, 0.06 mmol, 14% yield); elution with a 1 : 1 mixture of *n*-hexane and dichloromethane delivered an orange-coloured mixture (the NMR ^{1}H analysis indicated a mixture of two complexes); elution with pure dichloromethane afforded an orange-coloured fraction containing **4c** (0.053 g, 0.12 mmol, 29% yield). The second fraction was adsorbed on hydrated silica gel and submitted to a second chromatographic separation over hydrated silica gel/*n*-hexane (0 °C) with a 9 : 1 mixture of *n*-hexane and dichloromethane (0.5 l) affording thus a red containing **4b** (traces); elution with a 1 : 1 mixture of dichloromethane and *n*-hexane afforded a yellow fraction containing **4d** (0.032 g, 0.05 mmol, 12% yield). **4e**: HRMS (FAB$^+$) Calc. for $C_{38}H_{35}N_4O_3Mn$ (M$^+$): 725.125601. Found: 725.125605. Anal. Calc. for $C_{38}H_{34}N_2O_6Mn_2$: C 62.99, H 4.73, N 3.87. Found: C 63.31, H 4.94, N 3.65%. IR (CH_2Cl_2) ν(CO)/cm^{-1}: 2019 (s), 1992 (vs), 1944 (m), 1903 (s). δ_H ($CDCl_3$, 263 K) 8.07 (m, 3H), 7.43 (m, 1H), 7.04 (d, 1H, ^3J = 8.0), 6.79 (t, 1H, ^3J = 7.5), 6.75 (t, 1H, ^3J = 7.2), 6.70 (t, 1H, ^3J = 7.1), 6.64 (d, 1H, ^3J = 7.0), 6.59 (t, 1H, ^3J = 5.1), 6.28 (d, 1H, ^3J = 7.8), 5.65 (t, 1H, ^3J = 5.1), 5.05 (t, 1H, ^3J = 6.5), 4.94 (t, 1H, ^3J = 6.0), 4.33 (d, 1H, ^3J = 7.7), 4.27 (d, 1H, ^3J = 7.4), 1.42 (s, broad, 9H), 1.00 (s, 9H). δ_C ($CDCl_3$, 263 K) 232.0, 223.2, 222.1, 221.9 (3CO), 163.7, 158.4, 157.1, 146.5, 144.4, 139.3, 135.0, 134.7, 130.3, 128.2, 127.5, 126.5, 126.0, 125.8, 125.6, 124.6, 119.6, 116.1, 106.8, 97.9, 97.7, 82.6, 75.7, 72.5, 67.3, 39.6, 35.5, 30.9, 30.1 (3 C), 28.1. MS (FAB$^+$) *m*/*z* 725 (M$^+$), 640 (M − 3CO), 613 (M$^+$ − 2CO − Mn), 585 (M − 3CO − Mn), 557 (M − 4CO − Mn), 502 (M − 4CO − 2Mn). **4c**: Anal. Calc. for $C_{24}H_{21}N_2O_3Mn$: C 65.46, H 4.81, N 6.36. Found: C 65.10, H 4.79, N 6.40%. IR (*n*-hexane) ν(CO)/cm^{-1}: 2004 (vs), 1930 (s), 1915 (s). δ_H ($CDCl_3$, 263 K) 8.16 (d, 1H, ^3J = 5.1, $H_{pyrimidine}$), 8.09 (d, 1H, ^3J = 9.1, $H_{Ph\ coordinated}$), 7.97 (d, 1H, ^3J = 5.2, $H_{pyrimidine}$), 7.85 (d, 1H, ^3J = 8.5, $H_{Ph\ coordinated}$), 7.63 (t, 1H, ^3J = 7.9, $H_{Ph\ coordinated}$), 7.33 (t, 1H, ^3J = 7.5, $H_{Ph\ coordinated}$), 7.24 (d*, 1H, H_{Ph}), 6.83 (t, 1H, ^3J = 7.6, H_{Ph}), 6.69 (t, 1H, ^3J = 7.3, H_{Ph}), 6.63 (t, 1H, ^3J = 6.8, H_{Ph}), 6.58 (t, 1H, ^3J = 5.2, $H_{pyrimidine}$), 6.16 (d, 1H, ^3J = 7.6, H_{Ph}), 1.46 (s, 9H, *t*-Bu). δ_C ($CDCl_3$, 263 K) 230.4, 222.0, 221.3, 165.8, 158.4, 157.1, 143.9, 139.2, 134.5, 133.3 (2 C), 131.5, 126.7, 125.9, 125.2, 124.8, 118.9, 115.3, 94.0, 81.6, 39.3 (3 C), 28.2. **4d**: HRMS (FAB$^+$) Calc. for $C_{35}H_{36}N_4O_3Mn$ (M$^+$): 615.216775. Found: 615.216788. Anal. Calc. for $C_{35}H_{35}N_4O_3Mn{\cdot}1/2CH_2Cl_2$: C 64.89, H 5.52, N 8.53. Found: C 64.91, H 5.52, N 8.34%. IR (KBr) ν(CO)/cm^{-1}: 1997 (vs), 1919 (s), 1902 (s). δ_H ($CDCl_3$, 263 K) 7.96 (m, 1H), 7.86 (d, 1H, ^3J = 4.0), 7.52 (t, 1H, ^3J = 7.9), 7.34 (m, 3H), 7.20 (t, 1H, ^3J = 8.1), 7.12 (m, 2H), 7.01 (d, 1H, ^3J = 7.0), 6.88 (d, 1H, ^3J = 7.2), 6.71 (t, 1H, ^3J = 7.3), 6.61 (t, 1H, ^3J = 6.9), 6.56 (t, 1H, ^3J = 7.2), 6.25 (t, 1H, ^3J = 5.5), 6.16 (d, 1H, ^3J = 6.8), 3.50 (s, broad, 1H), 1.67 (s, 9H), 1.19 (s, 9H). δ_C ($CDCl_3$, 263 K) 236.4, 222.1, 221.6, 162.9, 159.1, 157.9, 155.2, 148.5, 143.6, 138.9, 134.2, 133.8, 132.9, 128.9, 128.8, 128.7, 128.6, 127.9, 126.6, 125.5, 124.5, 120.2, 118.3, 116.4, 104.1, 82.6, 78.6, 39.4, 38.2, 28.4 (6 C). MS (FAB$^+$): *m*/*z* 615 [M]$^+$, 530 [M − 3CO]$^+$, 475 [M − 3CO − Mn]$^+$. **4b**: IR (CH_2Cl_2) ν(CO)/ cm^{-1}: 2079 (w), 2004 (vs), 1985 (m), 1941 (m), 1916 (m). δ_H ($CDCl_3$, 263 K) 8.06 (d, 1H, ^3J = 4.7), 7.82 (m, 3H), 7.61 (d, 1H, ^3J = 8.2), 7.45 (t, 1H, ^3J = 7.8), 7.01 (t, 1H, ^3J = 7.7), 6.73 (t, 1H, ^3J = 7.5), 6.53 (t, 1H, ^3J = 7.2), 6.38 (t, 1H, ^3J = 5.5), 5.81 (d, 1H, ^3J = 6.8), 1.50 (s, 9H). δ_C ($CDCl_3$, 263 K) 230.7, 222.5, 219.1, 218.7, 214.1, 212.8, 212.5, 176.0, 165.8, 158.4, 158.2,

145.8, 139.9, 137.7, 131.0, 130.9, 129.0, 126.5, 126.0, 125.6, 116.4, 114.7, 104.1, 81.3, 39.2, 32.6 (3 C).

Bis(tricarbonylmanganese(I))(2,3-di-(η²-2′-(η¹-diphenylmethylene-κ*C*)phenyl)benzo[*g*]quinoxaline-κ*N*,κ*N*′), complex 6b. A solution of Ph_2CN_2 (500 mg, 2.57 mmol) in toluene (1 mL) was added dropwise to a boiling solution of **6a** (300 mg, 0.45 mmol) dissolved in a 10 : 1 mixture of *n*-hexane (10 mL) and toluene (1 mL) for 1 h. The colour of the medium changed from deep red to dark green within 40 min. The solvents were subsequently removed under reduced pressure and the residue dissolved in CH_2Cl_2. Silica gel was added to the resulting solution and the suspension was stripped of solvent. The coated silica gel was loaded on the top of a cooled SiO_2 column packed in dry *n*-hexane. Elution with a mixture of 30% CH_2Cl_2 in *n*-hexane allowed the recovery of a brownish mixture of unstable and unidentified compounds. Further elution with a 50% mixture of CH_2Cl_2 and *n*-hexane allowed the recovery of a dark green fraction containing **6b** as the major component. This fraction was stripped of solvents and the raw material was recrystallized thrice from CH_2Cl_2 and *n*-hexane to afford a pure sample (15 mg, 3.5% yield). Complex **6b**: HRMS (FAB⁺) Calc. for $C_{56}H_{34}N_2O_6Mn_2$: 940.117766. Found: 940.117780. IR (*n*-hexane) ν(CO)/cm^{-1}: 2002, 1935, 1912. δ_H ($CDCl_3$) 8.20 (s, 2H), 8.01 (dd, 2H, $^3J = 6.4$, $^4J = 3.2$), 7.71 (d, 4H, $^3J = 7.4$), 7.61 (dd, 2H, $^3J = 6.5$, $^4J = 3.2$), 7.38 (m, 6H), 7.30–7.13 (m, 10H), 6.80 (t*d, 2H, $^3J = 7.5$, $^4J = 1.0$), 6.68 (d, 2H, $^3J = 7.6$), 6.21 (t*, 2H, $^3J = 7.4$), 5.93 (t*, 2H, $^3J = 7.6$, $^4J = 1.2$). δ_C ($CDCl_3$, 263 K) 230.6, 220.8, 219.7, 146.4, 145.9, 134.9, 134.5, 133.8, 133.2 (broad), 133.1, 131.7, 131.2, 128.5 (broad, 2C), 128.3, 127.1, 126.5, 126.1, 125.3, 125.0, 123.9, 123.1, 115.6, 87.6, 75.8. MS (FAB⁺): *m*/*z* 940.8 [M]⁺, 855.8 [M − 3CO]⁺, 828.8 [M − 4CO + H]⁺, 801.0 [M − 5CO + H]⁺, 771.9 [M − 6CO − H]⁺, 717.0 [M − 6CO − Mn]⁺, 663.1 [M − 6CO − 2Mn + H]⁺.

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References

1 R. S. Hay and P. J. Pomery, *Aust. J. Chem.*, 1972, **25**, 2597–2603; W. Kaim, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 171–190; W. Kaim, *Angew. Chem.*, 1983, **95**, 201–221.
2 M. A. Petit, C. Clarisse and F. Templier, *J. Electrochem. Soc.*, 1993, **140**, 2498–2500; T. Kanbara, T. Inoue, K. Sugiyama and T. Yamamoto, *Synth. Met.*, 1995, **71**, 2207–2208; C. Giebeler, R. N. Marks, A. Bleyer, D. D. C. Bradley and S. Schrader, *Opt. Mater.*, 1998, **9**, 99–103; M. Thelakkat and H. W. Schmidt, *Polym. Adv. Technol.*, 1998, **9**, 429–442; M. B. Casu, P. Imperia, S. Schrader, B. Falk, M. Jandke and P. Strohriegl, *Synth. Met.*, 2001, **124**, 79–81; A. P. Kulkarni, Y. Zhu and S. A. Jenekhe, *Macromolecules*, 2005, **38**, 1553–1563.
3 K. B. Wiberg and T. P. Lewis, *J. Am. Chem. Soc.*, 1970, **92**, 7154–7160; J. E. O'Reilly and P. J. Elving, *J. Am. Chem. Soc.*, 1971, **93**, 1871–1879; R. S. Hay and P. J. Pomery, *Aust. J. Chem.*, 1971, **24**, 2287–2292; J. E. O'Reilly and P. J. Elving, *J. Am. Chem. Soc.*, 1972, **94**, 7941–7949; A. Minsky, Y. Cohen and M. Rabinovitz, *J. Am. Chem. Soc.*, 1985, **107**, 1501–1505; Y. Cohen, A. Y. Meyer and M. Rabinovitz, *J. Am. Chem. Soc.*, 1986, **108**, 7039–7044; L. Eberson and S. S. Shaik, *J. Am. Chem. Soc.*, 1990, **112**, 4484–4489; P. Zanello, M. Fontani, S. Z. Ahmed and C. Glidewell, *Polyhedron*, 1998, **17**, 4155–4162.
4 J. M. Fritsch, T. P. Layloff and R. N. Adams, *J. Am. Chem. Soc.*, 1965, **87**, 1724–1726; A. Grimison, A. Simpson, M. Trujillo Sanchez and J. Jhaveri, *J. Chem. Phys.*, 1969, **73**, 4064–4070; W. Kaim, *Inorg. Chim. Acta*, 1981, **53**, L151–L153; J. Simonet, M. Carriou and H. Lund, *Liebigs Ann. Chem.*, 1981, **9**, 1665–1673; W. Kaim, *J. Am. Chem. Soc.*, 1984, **106**, 1712–1716; S. Hasenzahl, W. Kaim and T. Stahl, *Inorg. Chim. Acta*, 1994, **225**, 23–34; M. Lucarini and G. F. Pedulli, *J. Organomet. Chem.*, 1995, **494**, 123–131.
5 N. Arsu and M. Aydin, *Angew. Makromol. Chem.*, 1999, **270**, 1–4.
6 P. N. Moorthy and E. Hayon, *J. Phys. Chem.*, 1974, **78**, 2615–2620; W. Kaim, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1767–1769; S. Swavey, M. C. Ghosh, V. Manivannan and E. S. Gould, *Inorg. Chim. Acta*, 2000, **306**, 65–69.
7 P. J. Pouwels, R. F. Hartman, S. D. Rose and R. Kaptein, *Photochem. Photobiol.*, 1995, **61**, 575–583; J. K. Song, N. K. Lee and S. K. Kim, *J. Chem. Phys.*, 2002, **117**, 1589–1594.
8 W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187–235; W. Bruns, W. Kaim, E. Waldhoer and M. Krejcik, *Inorg. Chem.*, 1995, **34**, 663–672; A. Klein, E. J. L. McInnes, T. Scheiring and S. Zalis, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2979–2984; C. Nervi, R. Gobetto, L. Milone, A. Viale, E. Rosenberg, D. Rokhsana and J. Fiedler, *Chem. Eur. J.*, 2003, **9**, 5749–5756.
9 R. Gross and W. Kaim, *Inorg. Chem.*, 1986, **25**, 498–506; J. W. M. Van Outersterp, F. Hartl and D. J. Stufkens, *Organometallics*, 1995, **14**, 3303–3310; S. E. Page and K. C. Gordon, *Inorg. Chem.*, 1998, **37**, 4452–4459; D. J. Berg, J. M. Boncella and R. A. Andersen, *Organometallics*, 2002, **21**, 4622–4631; R. L. Williams, H. N. Toft, B. Winkel and K. J. Brewer, *Inorg. Chem.*, 2003, **42**, 4394–4400.
10 A. De Cian, J. P. Djukic, J. Fischer, M. Pfeffer and K. H. Dötz, *Chem. Commun.*, 2002, 638–639.
11 C. Michon, J. P. Djukic, Z. Ratkovic, J. P. Collin, M. Pfeffer, A. de Cian, J. Fischer, D. Heiser, K. H. Dötz and M. Nieger, *Organometallics*, 2002, **21**, 3519–3535.
12 J.-P. Djukic, C. Michon, D. Heiser, N. Kyritsakas-Gruber, A. de Cian, K. H. Dötz and M. Pfeffer, *Eur. J. Inorg. Chem.*, 2004, 2107–2122.
13 D. M. Labrush, D. P. Eyman, N. C. Baenziger and L. M. Mallis, *Organometallics*, 1991, **10**, 1026–1033; J. L. Moler, D. P. Eyman, J. M. Nielson, A. M. Morken, S. J. Schauer and D. B. Snyder, *Organometallics*, 1993, **12**, 3304–3315; S. U. Son, S. S. Lee and Y. K. Chung, *J. Am. Chem. Soc.*, 1997, **119**, 7711–7715.
14 J. P. Djukic, A. de Cian and N. Kyritsakas-Gruber, *J. Organomet. Chem.*, 2005, **690**, 4822–4827.
15 The second reduction process is reportedly irreversible:H. Bock, A. John, K. Näther and K. Ruppert, *Helv. Chim. Acta*, 1994, **77**, 1505–1519.
16 C. Michon, J. P. Djukic, Z. Ratkovic and M. Pfeffer, *Tetrahedron Lett.*, 2002, **43**, 5241–5243.
17 H.-J. Meyer and T. Wolff, *Chem. Eur. J.*, 2000, **6**, 2809–2817; J. Armand, K. Chekir and J. Pinson, *Can. J. Chem.*, 1974, **52**, 3971–3980.
18 L. I. Smith and K. L. Howard, *Org. Synth.*, 1955, **Collect. vol. 3**, 351–352.
19 D. E. Pearson, *J. Am. Chem. Soc.*, 1950, **72**, 4169–4170; K. Ishiguro, M. Ikeda and Y. Sawaki, *J. Org. Chem.*, 1992, **57**, 3057–3066.
20 C. K. Fair, in *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*, Nonius, Delft, the Netherlands, 1990.