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Synthesis of cyclomanganated complexes derived from 2,5-diphenyl-1,3,4-oxadiazole and their reactivity with respect to 1,1-diphenyldiazomethane: Evidence for a fluxional trihaptobenzylic coordination mode

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Abstract

The cyclometallation of 2,5-diphenyl-1,3,4-oxadiazole with benzylpentacarbonylmanganese afforded the related mono- and binuclear complexes. The thermolytic coupling of 1,1-diphenyldiazomethane with monometallated 2,5-diphenyl-1,3,4-oxadiazole afforded substantial amounts of a new trihaptobenzylic complex. In the solid state, an X-ray diffraction analysis confirmed the coordination of manganese metal to one of the phenyl groups introduced by the 1,1-diphenyldiazomethane and to one of ligand's nitrogen centre. In solution, this trihaptobenzylic complex displays a fluxionality which is assumed to be related to the equilibration of its helical *Λ* and *Δ* enantiomers.

Keywords: Manganese; Diazoalkane; Insertion; X-ray diffraction; Metallacycles

1. 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 intended to be used in organic semi-conducting devices [2]. As proposed previously, the elaboration of ''electron nest-type'' architectures 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 could ensure to the material a high chemical stability, an essential feature for any intended applications as n-transporting layers in organic semiconductors. In a previous report [3], it was shown that electron-nest architectures could readily be built by the thermolytic coupling of bis-cyclomanganated heterocyclic derivatives, such as **1a**, with 1,1-diazoarylmethane leading to stable symmetric manganese-scaffolded triple decker architectures, such as **1b** (Eq. 1), exhibiting promising physicochemical properties [4,5].

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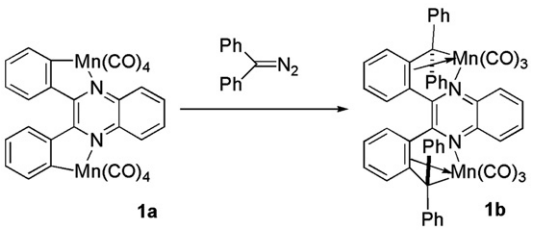


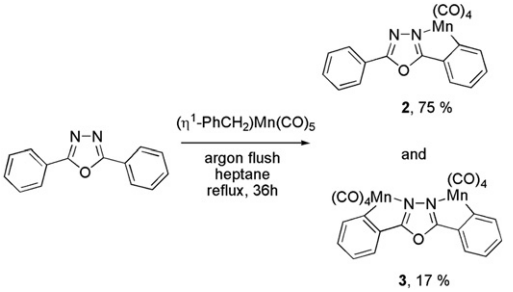
(1)

In this note we disclose an evaluation of the use of 2,5-diphenyl-1,3,4-oxadiazole, a well known electroactive n-transporting and fluorescent material [6], in the elaboration of oxadiazole-based triple-decker architectures through an investigation of its reaction with $(\eta^1\text{-PhCH}_2)\text{Mn(CO)}_5$ and the reactivity of its metallated derivatives towards Ph_2CN_2.

2. Results and discussion

2.1. Cyclomanganation of 2,5-diphenyl-1,3,4-oxadiazole with $(\eta^1\text{-PhCH}_2)\text{Mn(CO)}_5$

Ligand 2,5-diphenyl-1,3,4-oxadiazole was allowed to react with 2.5 equiv. of (η^1-benzyl)pentacarbonylmanganese in refluxing heptane for 36 h. After separation by chromatography over silica gel, the mono and bis-metallated complexes, i.e. compounds **2** and **3**, were recovered optimally, respectively, with 75% and 17% (Eq. 2).



(2)

The relatively low yield in **3** may be reasonably related to the peculiar steric cluttering expected in this bis-chelate. Strong interactions arise from short distances between $Mn(CO)_4$ fragments. The analysis of a structure of **3** (Fig. 1) determined by X-ray diffraction study confirmed the vicinity of the two equatorial carbonyl ligands, C(2)–O(2) and C(2a)–O(2a) from manganese atoms Mn and Mn(a) being separated by an interatomic distance O(2)...O(2a) of 2.904(3) Å. Such a steric hindrance confers a helical character illustrated by a value of 8° for dihedral angle Mn–N–N(a)–Mn(a). In the crystal lattice molecules are π-stacked, in a perfect parallel manner [7], with a mean

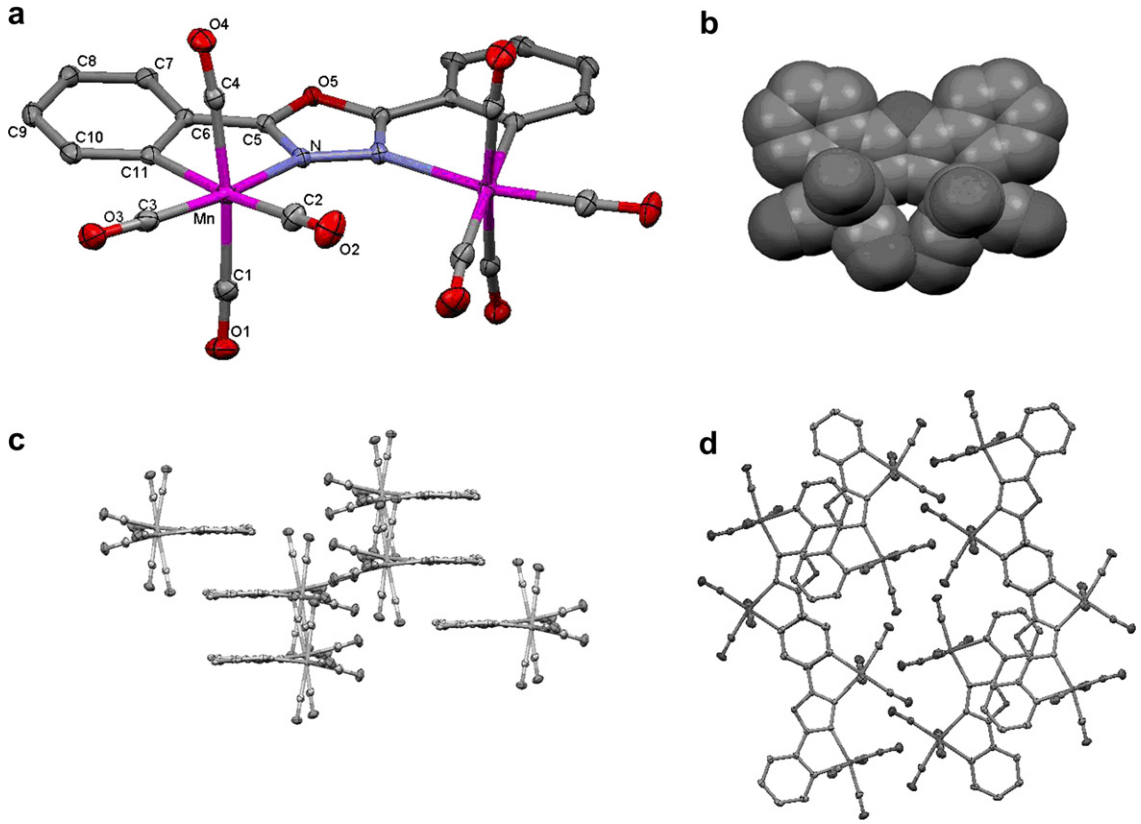


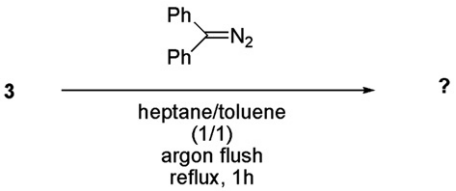
Fig. 1. (a) CSD-mercury diagram of the structure of **3**, ellipsoids are drawn at the 30% probability level; selected distances (Å), angles (°), and torsion angles (°) (index "a" refers to symmetry-related atoms, which have not been numbered here for convenience): Mn–N, 2.113(1); Mn–C(11), 2.086(2); Mn–C(1), 1.868(2); Mn–C(2), 1.846(2); Mn–C(3), 1.795(2); Mn–C(4), 1.860(2); N–N(a), 1.413(2); O(2)–O(2a), 2.904(3); C(6)–C(5)–N–Mn, 4.4; C(5)–N–Mn–C(11), 6.3; N–C(5)–C(6)–C(11), 2.0; N–Mn–C(11)–C(6), 7.6; Mn–C(11)–C(6)–C(5), 7.5; O(5)–C(5)–C(6)–C(7), 4.7; Mn–N–N(a)–Mn(a), 8.0; N(a)–N–Mn–C(2), 9.5; N–Mn–C(11), 79.59(5). (b) Space-filling diagram showing the contacts between vicinal $Mn(CO)_4$ fragments. (c) and (d) Side and top views of the molecular packing in the crystal lattice. Hydrogen atoms have been omitted for the sake of clarity.

inter-planar distance between the diphenyl-oxadiazolyl ligands amounting ca. 3.2 Å.

The IR spectra of complexes **2** and **3** display four bands (2 A_1, 1 B_1 and 1 B_2) for the stretching vibrations of the manganese carbonyl ligands. ^{13}C NMR spectra of **2** and **3** display only three peaks for the four carbonyl ligands at δ 219.9, 213.4, 211.5 ppm (two axial CO ligands) for **2** and at δ 219.8, 214.3, 212.4 ppm (two axial CO ligands) for **3**. Such pattern is typical of *cis*-$L_2Mn(CO)_4$ complexes as far as the metallacycle defines a symmetry plane that leads to the equivalence of the two axial carbonyl ligand.

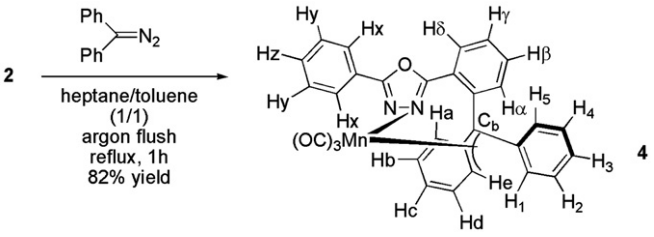
2.2. Thermolytic coupling with Ph_2CN_2

The reaction of complex **3** with Ph_2CN_2 (Eq. 3) proved to be sluggish. Whereas IR spectra of crude mixtures showed evidence of the diazoalkane consumption and probable generation of trihaptobenzylic species (ν_{CO} 2024, 2006, 1949, 1918 cm^{-1}), nothing but an air-sensitive and oily material was recovered upon chromatographic separation precluding further characterizations.



(3)

Nonetheless, refluxing complex **2** with Ph_2CN_2 in a (1/1) heptane/toluene mixture led to a new trihaptobenzylic complex **4**, isolated as an orange solid, in 82% yield after chromatographic purification (Eq. 4).



(4)

The X-ray diffraction analysis of a crystal of **4** (Fig. 2) revealed a quite unexpected coordination mode for the $Mn(CO)_3$ moiety. As opposed to other known pyridyl, quinolyl and quinoxalyl trihaptobenzylic manganese complexes, the phenyl ring comprising atoms C(19)–C(24) is

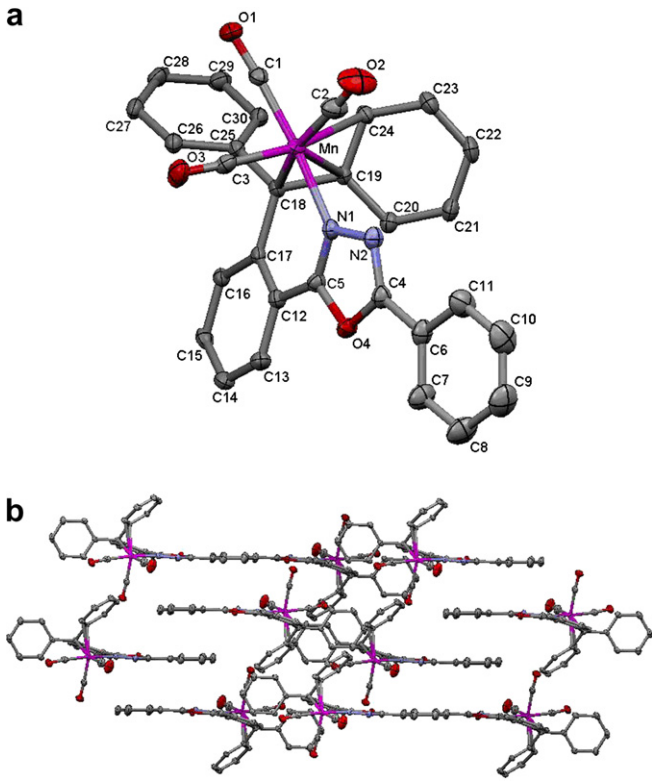


Fig. 2. (a) CSD-mercury diagram of the structure of **4**, ellipsoids are drawn at 50% probability level; disordered molecules of solvents and hydrogen atoms have been omitted for the sake of clarity; selected distances (Å), angles (°), and torsion angles (°): Mn–N(1), 2.033(3); Mn–C(18), 2.165(3); Mn–C(19), 2.275(3); Mn–C(24), 2.420(7); C(19)–C(20), 1.429(4); C(20)–C(21), 1.371(4); C(21)–C(22), 1.406(5); C(22)–C(23), 1.365(5); C(23)–C(24), 1.417(4); C(24)–C(19), 1.418(4); N(1)–N(2), 1.408(4); C(17)–C(18), 1.509 (4); C(18)–C(19), 1.479(4); C(20)–C(19), 1.429(4); C(19)–C(24), 1.418(4); C(21)–C(20), 1.371(4); C(22)–C(21), 1.406(5); C(23)–C(22), 1.365(5); C(24)–C(23), 1.417(4); (N(1),N(2),C(4),O(4),C(5))–(C(19),C(20),C(21),C(22), C(23),C(24)), 3.900(7). C(17)–C(18)–C(19), 117.0(3); C(18)–Mn–C(19), 38.8(1); C(19)–Mn–C(24), 34.9(4). N(1)–C(5)–C(12)–C(17), 14.6; C(5)–C(12)–C(17)–C(8), 0.8; C(12)–C(17)–C(18)–C(19), 56.7; C(17)–C(18)–C(19)–C(20), 1.3. (b) Side view of the molecular packing in the crystal lattice.

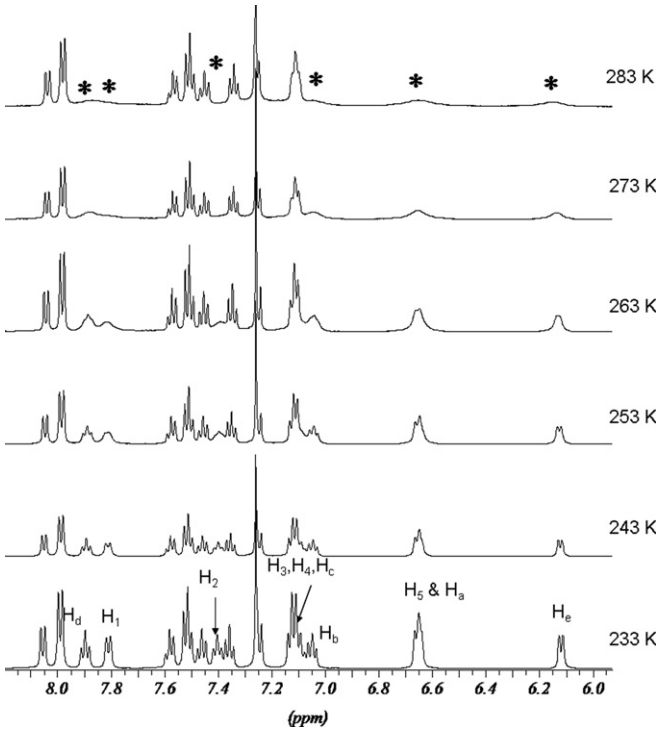
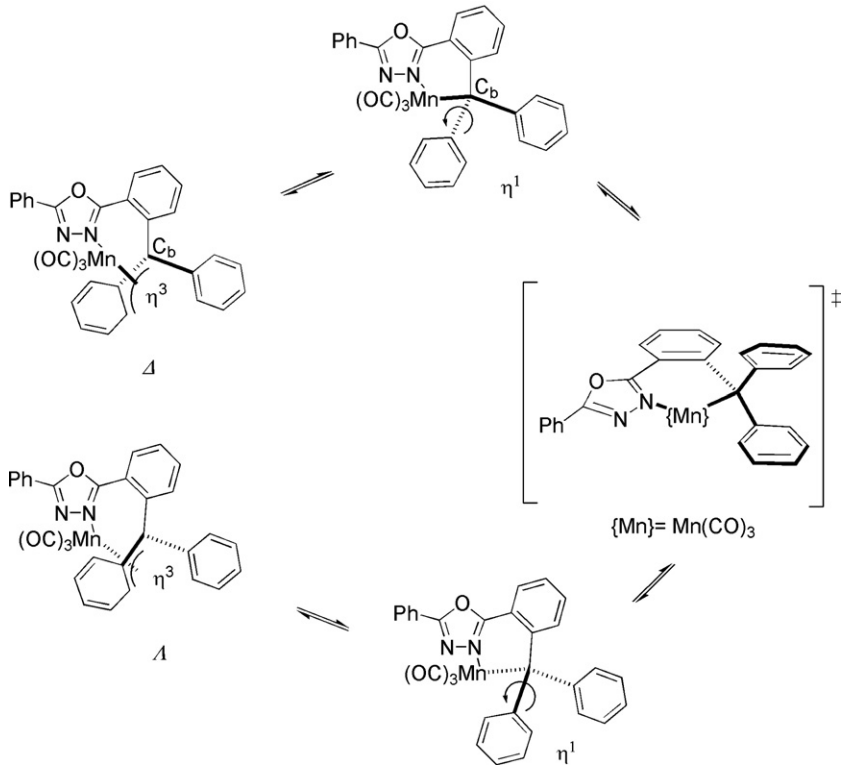


Fig. 3. Variable temperature ^1H NMR (500 MHz) experiments for **4** in $CDCl_3$.

not superimposed to the diazaoxazole ring but stands close to it, in a shifted position and it is bonded to the $Mn(CO)_3$ fragment in a η^2 fashion. The manganese atom is also part of a nearly planar 6-membered metallacycle comprising atoms Mn, N(1), C(5), C(12), C(17) and C(18). The manganese centre sits in a slightly distorted octahedral coordination geometry wherein the four equatorial positions are occupied by atoms C(1), C(3), N(1) and C(24). Axial positions are occupied by atoms C(2) and C(18).

A standard decrease of the Mn-to-C interatomic distance is observed for the manganese-benzylic fragment following the order Mn–C(24) > Mn–C(19) > Mn–C(18). Such pattern is frequently encountered with tricarbonylmanganese (η^2; η^1-benzyl) [8,9a] and (η^3-allyl) [9b] complexes. Interatomic distances C(20)–C(21) and C(22)–C(23) are slightly shorter than C(19)–C(20) and C(21)–C(22), suggesting thus a partial lift of conjugation as a result of the coordination to the manganese in the η^2 mode. It is worthy to note that the packing scheme of the analyzed crystal favours a perfectly parallel intermolecular π-stacking of the phenyl-oxadiazolyl tails of compound **4** with an inter-annular distance amounting ca. 3.5 Å. The unit cell comprises two inversion centre-related molecules of **4** having opposite configurations and disordered molecules of water and CH_2Cl_2.

The IR spectrum of complex **4** in solution displayed three intense bands corresponding to the stretching vibrations of the carbonyl ligands of the *fac*-$Mn(CO)_3$ fragment located in an asymmetric coordination environment. The ^{13}C NMR spectrum of **4** at 263 K clearly displayed the three peaks for carbonyl ligands (229.8, 221.3 and 219.3 ppm); other signals related to the ligand's backbone appeared between 163.6 and 66.4 ppm. ^1H NMR experiments at sub-ambient temperatures were necessary to overcome dynamic effects for, at room temperature, the spectrum was mostly unresolved and appeared as a composite combination of broad signals and sharp multiplets arising from protons H_x–H_z and H_α–H_δ (Fig. 3). A ^1H–^1H COSY experiment carried out at 243 K, a temperature at which slow exchange rate was expected within ^1H NMR time scale, enabled a full assignment of the signals (cf. Appendix A). The origin of the observed dynamic behaviour was further investigated at 243 K by carrying out a ^1H–^1H ROESY experiment (cf. Appendix A). This established a clear connection between protons of the manganese-bound π-coordinated phenyl group. For instance, it was noticed that protons H_a and H_e, and H_b and H_d were mutually correlated by intense cross-peaks revealing a *mutual exchange* between these two *ortho* and two *meta* positions. This mutual exchange most probably results from a formal rotation of the η^2 coordinated phenyl group, a process which should involve two elementary steps (Scheme 1): (1) the shift of the $Mn(CO)_3$ moiety from a η^2–η^1 to a η^1 coordination mode, and (2) the rotation of the phenyl group around the C_{ipso}–H_c axis and its recoordination. Moreover, it was noticed that the signals arising from the *exo*-phenyl group (viz. H_1–H_5) also happened to significantly broaden upon raising the temperature above



Scheme 1.

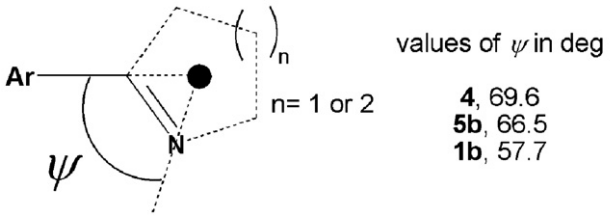
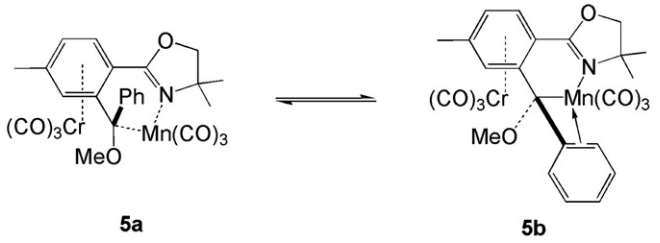


Fig. 4. Intra-annular angle ψ is defined by the interception of the lines connecting the ring's centroid to the carbon atom bound to the vicinal aryl fragment and to the nitrogen atom bound to manganese.

243 K, which suggested a secondary exchange process. A rationale for this would be the *equilibration* of the *Λ* and *Δ* helical enantiomers of racemic **4** (Scheme 1), which should be enabled by the partial de-coordination of the Mn center evidenced above. This accounts reasonably for the highly broadened signals observed at 283 K assigned to the two benzylic carbon-bound phenyl groups. Unfortunately, the ROESY experiment did not show cross peaks connecting protons H_1–H_5 and H_a–H_e probably because of the low exchange rate of this process at 243 K.

Worthy to note, a similar fluxional behaviour was already observed in solution with two isomeric compounds derived from 4,4-dimethyl-2-[(η^6-4-tolyl)tricarbonylchromium]-2-oxazoline, i.e. compounds **5a** and **5b**, which were shown to interconvert readily in solution [10] (Eq. 5). It was originally stated that the flexibility of the oxazolyl ring could account for the propensity of the two isomers to interconvert in solution.



(5)

We assume that the fluxionality reported here and in our previous work is most probably a consequence of the geometric features introduced by the oxazolyl and oxadiazolyl ligands. Such five-membered ligands possess a large intra-annular angle ψ (Fig. 4) of ca. 68° as compared to ca. 58° in pyridyl [8,10] and quinoxalyl related ligands [4], which might contribute both in increasing the flexibility and enabling the establishment of a nearly planar six-membered manganacycle as observed in **4** and **5b** [10].

3. Conclusion

Biscyclomanganated aromatic compounds are generally readily accessible [4,11] by the thermolysis of alkylpentacarbonylmanganese compounds in the presence of an aromatic ligand whenever electronic properties of the host ligand and steric hindrance do not preclude the pre-coordination of the manganese in the early stages of the metallation reaction or do not lead to ligand alteration [12]. We have demonstrated here that the metallation of 2,5-diphenyl-1,3,4-oxadiazole with (η^1-benzyl)pentacarbonylmanganese was effective although producing a mixture of mono- and binuclear complexes **2** and **3**. The yields and ratio of the latter products are deemed to be mostly determined by steric entanglement. This result somewhat complements the conclusions drawn by other authors on the mono-palladation [13] and mono-iridation [14] of oxadiazoles. In the light of the observations made with **4**, the failure of the thermolytic coupling of 1,1-diphenyldiazomethane with **3** to produce a persistent and stable dinuclear analog could be explained by a possible high fluxional character. Indeed, the coordinative *hemilability* of the 2,5-diphenyl-1,3,4-oxadiazolyl ligand, evidenced here with **4**, could expose more critically the Mn centre to external oxidizing agents as its coordination sphere would constantly be partly unsaturated especially if molecular entanglement is marked. Nonetheless, this peculiar feature, which seemingly precludes further use of oxadiazole-based chelates in the elaboration of *rigid* triple-decker "electron nests", might be of interest in homogeneous catalysis.

4. Experimental

4.1. General

All experiments were carried out under a dry atmosphere of argon with distilled, dry and degassed solvents. 2,5-Diphenyl-1,3,4-oxadiazole was purchase from Aldrich Chem. Co. and used without further purification. 1,1-Diphenyldiazomethane [15] was prepared by oxidation of the corresponding hydrazone with yellow HgO at room temperature. NMR spectra were acquired on Bruker Avance 500 (^{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 constants are expressed in Hz. IR spectra were measured with a Perkin–Elmer FT spectrometer. Mass spectra (FAB+) were recorded at the Service of Mass Spectrometry of University Louis Pasteur and at the Analytical Centre of the Chemical Institute of the University of Bonn (EI). Elemental analyses (reported in% mass) were performed at the Service d'Analyses of the "Institut de Chimie de Strasbourg" and at "Institut Charles Sadron" in Strasbourg.

4.2. Procedure for X-ray diffraction analysis and structure resolution for 3 and 4

Acquisition and processing parameters are provided in Table 1. Reflections were collected with a Nonius Kappa CCD diffractometer using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å). The structures of **3** and **4** were solved using direct methods, they were refined against $|F|$ and for all pertaining computations, the Nonius

Table 1
Table of acquisition and refinement parameters for structures **3** and **4**

Compound	**3**	**4**
Formula	$C_{22}H_8Mn_2N_2O_9$	$2(C_{30}H_{19}MnN_2O_4)$-$CH_2Cl_2H_2O$
Molecular weight	554.19	1155.82
Crystal system	Monoclinic	Triclinic
Space group	$C\,2/c$	$P\bar{1}$
a (Å)	11.2799(2)	8.8290(3)
b (Å)	22.4877(6)	10.1306(3)
c (Å)	10.0822(2)	16.1716(5)
α (°)		92.107(5)
β (°)	123.160(5)	99.818(5)
γ (°)		99.515(5)
V (Å^3)	2140.9(1)	1402.50(7)
Z	4	1
Color	Yellow	Orange
Crystal dimension (mm)	$0.14\times0.10\times0.08$	$0.20\times0.20\times0.14$
D_{calc} (g cm^{-3})	1.72	1.37
F_{000}	1104	592
μ (mm^{-1})	1.239	0.606
Minimum and maximum transmission	0.835/0.985	0.9240/1.0000
T (K)	173	173
Scan mode	'phi scans'	'phi scans'
hkl Limits	−15, 15/−28, 31/−14, 14	0, 12/−14, 14/−22, 22
θ Limits (°)	2.5/30.01	2.5/30.07
Number of data measured	5670	8162
Number of data with $I > 3\sigma(I)$	2328	5648
Number of variations	159	370
R	0.029	0.057
R_w	0.044	0.076
Goodness-of-fit	1.050	1.053
Largest peak in final difference (e Å^{-3})	0.276	1.268

OpenMoleN package was used [16]. In structure **4**, highly disordered solvating molecules of CH_2Cl_2 and H_2O were not refined.

*4.3. Synthesis of complex **3**, [2,5-(diphenyl-κC$^{2'}$,κC$^{2''}$)]-1,3,4-oxadiazole-(κN^1,κN^2)bis(tetracarbonylmanganese(I)), and complex **2**, [2,5-(phenyl-κC$^{2'}$,phenyl)]-1,3,4-oxadiazole-(κN^1)(tetracarbonylmanganese(I))*

2,5-Diphenyl-1,3,4-oxadiazole (0.3 g, 1.35 mmol) and benzylmanganesepentacarbonyl (0.46 g, 1.61 mmol, 1.2 equiv.) were refluxed in distilled *n*-heptane (15 mL) during 12 h under a gentle stream of argon. An additional amount of benzylmanganesepentacarbonyl (0.5 g, 1.75 mmol, 1.3 equiv.) was then added and the resulting mixture was again refluxed for 24 h. After cooling to room temperature, the solvent was removed under vacuum. Chromatography on silica gel (40–63 μm) at 5 °C allowed to separate a yellow band containing complex **3** eluted with a 9:1 mixture of *n*-hexane and dichloromethane (1 L) (0.131 g, 0.236 mmol, 17% yield). A pale yellow band containing complex **2** was eluted with a 8:2 mixture of *n*-hexane and dichloromethane (0.395 g, 1.01 mmol, 75% yield).

*Compound **2***. HRMS (FAB$^+$) calcd. for $C_{18}H_9N_2O_5Mn$: 387.989193. Found: 387.989193. MS (FAB$^+$): *m/z* 388 (M)$^+$, 361 (MH–CO)$^+$, 332 (M–2CO)$^+$, 304 (M–3CO)$^+$. Anal. calcd. for $C_{18}H_9N_2O_5Mn$: C, 55.69; H, 2.34; N, 7.22. Found: C, 55.33; H, 2.35; N, 7.22%. IR (KBr) ν_{CO} (cm^{-1}): 2082 (w), 1995 (s), 1990 (s), 1945 (m). ^{1}H NMR ($CDCl_3$): δ 8.11 (d, 2H, $^3J = 6.3$), 8.05 (d, 1H, $^3J = 7.5$), 7.78 (d, 1H, $^3J = 7.7$), 7.58 (m, 3H), 7.40 (t, 1H, $^3J = 7.3$), 7.25 (t*, 1H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 219.8 (CO), 214.3 (CO), 212.4 (2CO), 177.9, 170.9, 165.7, 142.5, 132.6, 131.8, 129.7, 129.4 (2C), 126.9 (2C), 125.1, 124.5, 123.1.

Compound **3**: Anal. calcd. for $C_{22}H_8N_2O_9Mn_2$: C, 47.68; H, 1.46; N, 5.05. Found: C, 47.57; H, 1.31; N, 5.06%. IR (KBr) ν_{CO} (cm^{-1}): 2087 (w), 2009 (s), 1998 (s), 1934 (m). ^{1}H NMR ($CDCl_3$): δ 8.10 (d, 2H, $^3J = 7.3$), 7.83 (d, 2H, $^3J = 7.7$), 7.45 (t, 2H, $^3J = 7.4$), 7.30 (t, 2H, $^3J = 7.5$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 219.9 (CO), 213.4 (CO), 211.5 (2 CO), 177.5, 171.2, 142.3, 132.5, 129.9, 125.9, 124.9.

*4.4. Synthesis of complex **4**, [1″2″2′: η-2′-(diphenylmethylene)-phenyl]-5-phenyl-1,3,4-oxadiazole-(κN)-tricarbonylmanganese (**I**)*

Complex **2** (0.153 g, 0.39 mmol) was dissolved in a mixture of 5 mL of heptane and 5 mL toluene. The resulting solution was brought to reflux under a stream of argon and a solution of 1,1-diphenyldiazomethane (0.152 g, 0.78 mmol) in 2 mL toluene was added dropwise over 25 min. The resulting mixture was heated for an additional period of 35 min and cooled to room temperature. Solvents were evaporated under reduced pressure and the raw mixture separated by flash chromatography over silica gel/*n*-hexane (6 °C). A 6:4 mixture of *n*-hexane and dichloromethane eluted a band containing **4**, which was recovered as a moderately air-sensitive orange solid (0.168 g, 0.32 mmol, 82% yield) upon evaporation of the volatiles.

HRMS (FAB$^+$) calculated for $C_{30}H_{19}N_2O_4Mn$ (M): 526.072525. Found: 526.072529. MS (FAB$^+$): *m/z* 527 (MH)$^+$, 470 (M–2CO)$^+$, 442 (M–3CO)$^+$, 387 (M–3CO–Mn)$^+$. Anal. calcd. for $C_{30}H_{19}N_2O_4Mn$: C, 68.58; H, 3.45; N, 5.33. Found: C, 67.57; H, 3.59; N, 5.26%. IR (KBr) ν_{CO} (cm^{-1}): 2004 (vs), 1917 (s), 1892 (s). IR (CH_2Cl_2) ν_{CO} (cm^{-1}): 2006 (vs), 1918 (s), 1906 (s). ^{1}H NMR ($CDCl_3$, 233 K): δ 8.05 (d, 1H, H_α, $^3J = 7.8$), 7.99 (d, 2H, H_x, $^3J = 7.5$), 7.90 (t, 1H, H_d, $^3J = 7.5$), 7.81 (d, 1H, H_1, $^3J = 7.8$), 7.58 (t, 1H, H_z, $^3J = 7.3$), 7.51 (t, 2H, H_y, $^3J = 7.6$), 7.46 (t, 1H, H_β, $^3J = 7.5$), 7.40 (t, 1H, H_2, $^3J = 7.2$), 7.36 (t, 1H, H_γ, $^3J = 7.5$), 7.24 (d*, 1H, H_δ), 7.11 (m, 3H, $H_3 + H_4 + H_c$), 7.05 (t, 1H, H_b, $^3J = 7.5$), 6.66 (d*, 2H, $H_5 + H_a$), 6.12 (d, 1H, H_e, $^3J = 7.1$). ^{13}C {^{1}H} NMR ($CDCl_3$, 263 K): δ 229.8, 221.3, 219.3, 163.6, 162.0, 150.0, 149.8, 136.7, 136.3, 132.6, 132.5, 132.4, 132.0, 129.2 (2C), 129.0, 127.9, 127.7, 127.6, 127.1 (2C), 126.4, 125.5, 125.0, 124.9, 122.1, 119.2, 116.3, 90.2, 66.4.

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Appendix A. Supplementary material

CCDC 623544 and 623545 contain the supplementary crystallographic data for **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.007.

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