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Unprecedented ligand anti-bis-benzylation upon thermolytic treatment of 2,3-diphenylbenzo[g]quinoxaline with (η^1-benzyl) pentacarbonylmanganese

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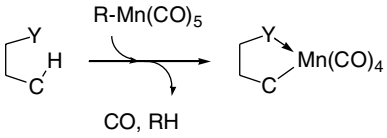
Abstract

The treatment of 2,3-diphenylbenzo[g]quinoxaline with $PhCH_2Mn(CO)_5$ in boiling *n*-heptane affords substantial amounts of a biscyclomanganated 5,10-anti-bis-benzylation product, which structure was assessed by X-ray diffraction analysis. In toluene and under similar experimental conditions, the formation of the latter is inhibited and the major product is the corresponding bis-cyclomanganated 2,3-diphenylbenzo[g]quinoxaline. The bis-benzylation reaction seemingly results from a trapping of benzyl radicals formed upon homolytic cleavage of the C–Mn bond in $PhCH_2Mn(CO)_5$ by the metallated 2,3-diphenylbenzo[g]quinoxaline.

Keywords: Manganese; N ligands; Crystal structures; Helical structures; Radicals

1. Introduction

It is well established that the treatment of ligand appended arenes with alkylmanganesepentacarbonyl complexes Eq. (1) may lead to the formation of [C,Y] heterochelates of $Mn(CO)_4$ (Y being a two electron donor ligand) [1]. These manganacyclic complexes have been subjected to a wide range of metal-centered transformations mostly involving insertion of electron-unsaturated moieties into the C–Mn bond [2].



(1)

The mechanism of this C_{Ar}–H bond activation reaction has been investigated by many authors, in various ways and often led to divergent conclusions as to the real nature of the intermediates [3]. According to Rourke and co-workers [4], the failure to establish a consistent kinetic law stems from the absence of a *clearly defined* rate determining step. In fact, the behaviour of $RMn(CO)_5$ has not much been investigated in the conditions used for cyclometallation. Although preliminary ligand coordination to the Mn center upon substitution of one CO ligand may be accepted as the reaction's first step, the fate of the resulting putatively labile $(L)(R)Mn(CO)_4$ species has never been addressed. Even though it is likely that an homolytic cleavage of the C–Mn bond yielding a pair of reactive alkyl and $(L)(CO)_4Mn$ radicals may take place [5], the importance of radicals in the ortho-metallation process has not yet been established. In this article, we report the unprecedented trapping of benzyl radicals in the course of the double cyclomanganation of 2,3-diphenylbenzoquinoxaline with $PhCH_2Mn(CO)_5$ and show that the bis-*anti*-benzylation reaction is sensitive to the nature of the solvent.

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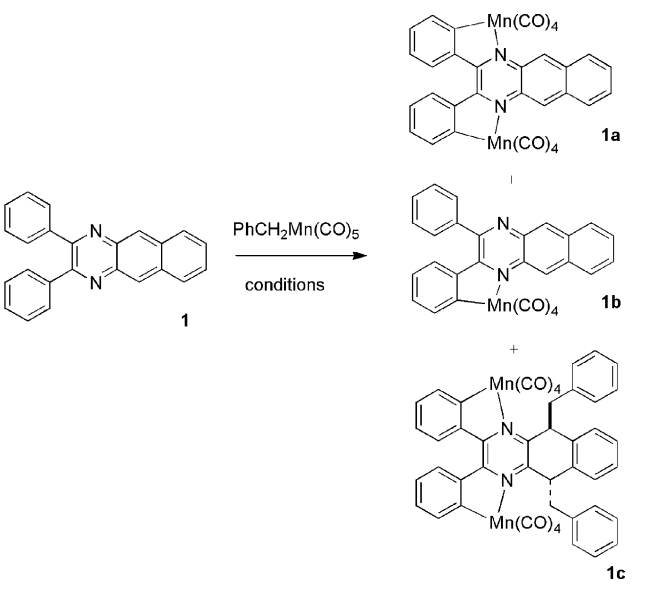
2. Results and discussion

2.1. The manganation of 2,3-diphenylbenzo[g]-quinoxaline 1

The treatment of **1** with 3 equiv. of $PhCH_2Mn(CO)_5$ Eq. (1) in a boiling mixture of *n*-hexane and benzene for 8 h afforded essentially the mono-manganated compound **1b** in 51% yield.



(2)

A similar experiment carried out in boiling toluene for 14 h with 2 equiv. of $PhCH_2Mn(CO)_5$ afforded essentially complex **1a** in 41% yield, which pro-helical molecular structure (Fig. 1) was confirmed by X-ray diffraction analysis (vide infra).

When the reaction of **1** [6] with $PhCH_2Mn(CO)_5$ was carried out in boiling *n*-heptane for 18 h, the reaction afforded minute amounts of **1a**, $Mn_2(CO)_{10}$ and significant amounts of a new compound **1c**, which C_2 symmetric structure was ascertained by NMR spectroscopy and X-ray diffraction analysis. An ORTEP diagram of the structure of **1c** is displayed in Fig. 2 (vide infra). Compound **1c** stems with certainty from the anti-double addition of a benzyl radical [7] to the central aromatic ring of the benzoquinoxaline at the 5 and 10 positions yielding the corresponding substituted pyrazine complex. The most plausible origin of the benzyl radical is the heat-promoted homolytic cleavage of the C–Mn bond [8] in $PhCH_2Mn(CO)_5$ or its coordinatively unsaturated tetracarbonyl derivatives. It is well known that the latter readily converts to $Mn_2(CO)_{10}$ and dibenzyl upon long periods of heating in aliphatic solvents [9] or upon irradiation [10]. The benzyl radical has a well documented propensity to attack activated aza-heterocycles [11]. However, the case reported herein is unprecedented as it involves a double addition of the $PhCH_2$ radical to an heterocycle, which could follow the reaction scheme drawn in Scheme 1.

At this stage, the inhibition of the formation of **1c** in toluene is not clear; we speculate that toluene might promote the scrambling of the benzyl radical via a predominant hydrogen abstraction process [12].

2.2. Structural characterization of 1a and 1c

An ORTEP diagram of **1a** is displayed in Fig. 1 beside two projections showing the stacking of the aromatic systems in the crystal lattice. Acquisition parameters and refinement data for all the structures presented herein are gathered in Table 1. Worthy to note, compound **1a**, which can be considered as a metalla and azabenzo analogue of its parent pentahelicene, exists under two forms in the crystal lattice, e.g., the inversion center-related helical *M* and *P* enantiomers. The helical orientation of the molecule stems obviously from the steric hindrance residing between vicinal phenylene moieties essentially at the C(28) and C(13) atoms and can be quantified by the interplanar phenylene–phenylene angle, which amounts 63.7°. It is worthy to note that this angle is larger than in the "all-carbon" parent [5] helicene – or 3,4-5,6-dibenzophenanthrene – (47.3°) [13] or 5,10-dihydro-benzo[a]indeno[2,3-c]fluorene (10.2°) [14]. This helical distortion entails a relatively important folding of the diaza-heterocycle C(26)–C(15)–N(1)–C(16)–C(25)–N(2) with the largest atomic shifts from the mean plane residing at atoms C(26) (+0.104(4) Å) and C(15) (−0.115(4) Å). In the crystal lattice, molecules of **1a** are π-stacked almost in a parallel head-to-tail manner with an alternation of *M* and *P* enantiomers: the angle between the quinoxalyl planes of two related enantiomers amounts ca. 2°. The mean interplanar distance is 3.5 Å.

A similar trend can be drawn for **1c**, which is also helical with an interplanar phenylene–phenylene angle of 55.4° (Fig. 2). The pyrazylene moiety deviates significantly from planarity with the largest atomic shifts from the mean plane showing at C(9) (−0.142(5) Å), C(16) (+0.132(5) Å), C(23) (+0.099(5) Å) and C(32) (−0.107(6) Å). The phenyl moieties of the benzyl groups are proximal to the polycyclic fragment seemingly to minimize steric interaction with the $Mn(CO)_4$ fragment: they define an interplanar angle with the central ring C(23)–C(24)–C(25)–C(30)–C(31)–C(32) amounting ca. 61°. This arrangement does not prevent the free motion of the benzyl group though. In the NMR time scale, the five phenyl protons resonate in $CDCl_3$ as three separate signals at δ 6.86 (t*, 2H), 6.64 (t*, 4H), 5.68 (d, 4H) ppm.

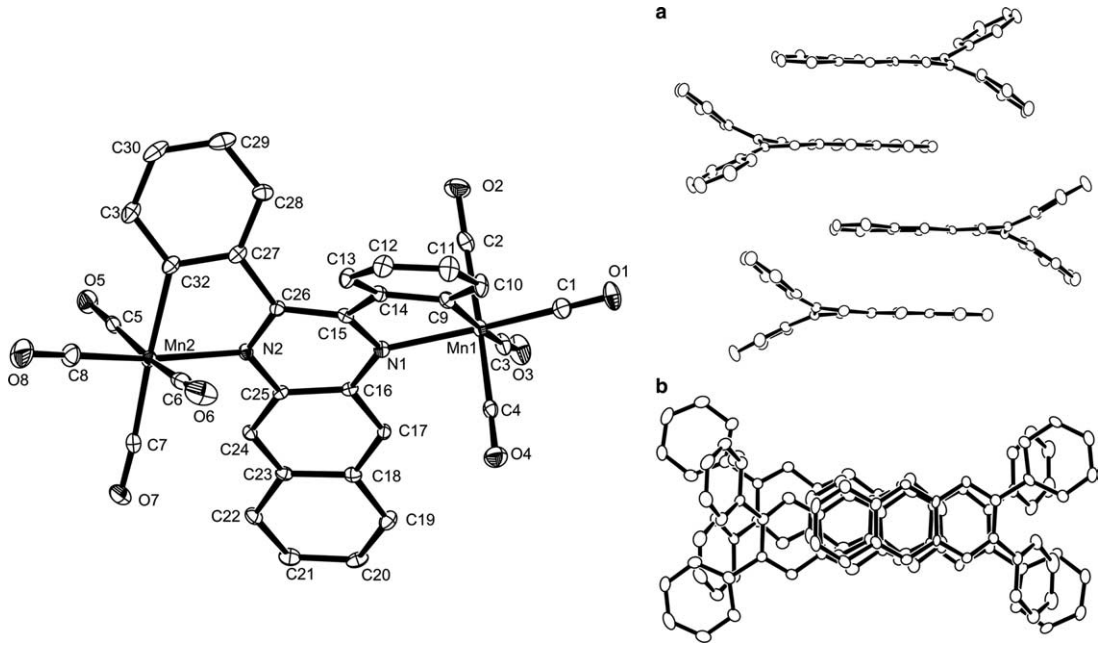


Fig. 1. Left: ORTEP diagram of complex **1a** displayed at 30% probability level. Hydrogen atoms have been omitted for clarity purpose. Interatomic distances (Å): C(13)–C(28), 3.181(9); Mn(2)–N(2), 2.100(4); C(13)–C(27), 3.297(8); Mn(2)–C(32), 2.037(5); Mn(1)–N(1), 2.120(4); Mn(1)–C(9), 2.058(5); C(14)–C(27), 3.217(9); C(14)–C(28), 3.206(9); C(14)–C(32), 4.562(9). Torsion angles (°): N(1)–C(15)–C(26)–N(2), 5.6; C(28)–C(27)–C(26)–C(15), 16.4; C(27)–C(26)–C(15)–C(14), 34.5; C(26)–C(15)–C(14)–C(13), 25.9. Right: (a) side view of the π-stacking in the crystal lattice; (b) top view showing the alignment of the heterocyclic units; $Mn(CO)_4$ fragments and hydrogen atoms have been omitted for clarity.

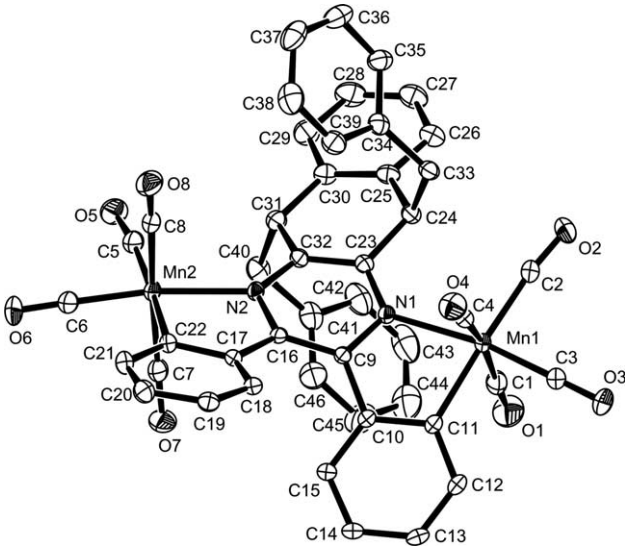
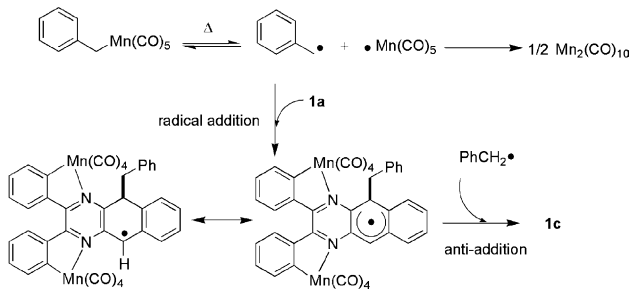


Fig. 2. ORTEP diagram of complex **1c** displayed at 30% probability level. Hydrogen atoms and molecules of CH_2Cl_2 have been omitted for clarity purpose. Interatomic distances (Å): Mn(1)–C(11), 2.042(6); Mn(1)–N(1), 2.177(5); C(16)–C(9), 1.409(7); C(23)–C(32), 1.397(7); C(24)–C(33), 1.563(9); C(31)–C(32), 1.508(7); C(23)–C(24), 1.510(8). Interatomic angles and torsion (°): N(1)–Mn(1)–C(11), 79.56(19); N(2)–Mn(2)–C(22), 80.2(2); C(17)–C(16)–C(9)–C(10), 32.0(8).



Scheme 1.

3. Conclusions

In summary, our results show a new aspect of the cyclomanganation reaction which might lead to interesting applications in radical-mediated synthesis. At this stage, it is not possible to anticipate which type of heterocyclic ligand might undergo similar homolytic radical additions since in many other reported cases of double metallation of phenyl substituted quinoxaline and pyrimidine derivatives such a side reaction was not noticed [2n,2o]. The therein reported reaction bears interesting similarities with the one described by Iwamura et al. [15], who observed the formation of a 9,10 dibenzylation adduct to anthracene upon thermal treatment of the latter with dibenzylmercury. There are other earlier reports [16] in the literature which document the trapping of benzyl radicals by anthracene. This allows us to propose that benzyl radicals do form in the course of the cyclomanganation reaction of **1** and that they can be trapped by **1a**.

Table 1
Acquisition[a] and refinement data for the X-ray diffraction analyses of compounds **1a** and **1c**

Compound	**1a**	**1c** · $2CH_2Cl_2$
Formula	$C_{64}H_{28}Mn_4N_4O_{16}$	$C_{46}H_{28}Mn_2N_2O_8 \cdot 2\ CH_2Cl_2$
Molecular weight	1328.71	1016.49
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	16.7514(2)	15.3761(2)
b (Å)	22.0204(4)	12.2420(2)
c (Å)	14.9158(3)	24.0031(4)
β (°)	94.353(5)	97.238(5)
V (Å^3)	5486.2(2)	4482.2(1)
Z	4	4
Color	Orange	Orange
Crystal dimension (mm)	$0.14 \times 0.08 \times 0.04$	$0.20 \times 0.18 \times 0.08$
D_{calc} (g cm^{-3})	1.61	1.51
F_{000}	2672	2064
μ (mm^{-1})	0.979	0.859
hkl limits	−23, 23/−30, 30/−20, 20	−21, 21/−15, 17/−33, 33
θ limits (°)	2.5/29.99	2.5/30.01
Number of data measured	16254	21449
Number of data with $I > 3\sigma(I)$	8160	7243
Number of variables	793	598
R	0.070	0.084
R_w	0.085	0.101
Goodness-of-fit	1.463	1.146
Largest peak in final difference (e Å^{-3})	0.903	1.368

[a] Reflections were collected at 173 K with a Nonius KappaCCD diffractometer using the Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å).

Further investigations are underway to probe the reactivity of both **1a** and **1c**.

3.1. 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 constants 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 at the Analytical Center 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 the analytical center of the "Institut Charles Sadron" in Strasbourg. Chromatographic separations were performed 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. Purifications required the use of deactivated silica prepared by suspending 200 g of SiO_2 in a mixture of distilled acetone and water (4% in weight); the resulting silica gel was washed with 200 mL of *n*-hexane and dried under reduced pressure prior to use.

3.2. Manganation of 2,3-diphenylbenzoquinoxaline *1* in *n*-heptane

A solution containing 2,3-diphenylbenzoquinoxaline **1** (1 g, 3 mmol) and $PhCH_2Mn(CO)_5$ (4.32 g, 15 mmol) in *n*-heptane (20 mL) was refluxed for 18 h. During that time the colour of the reaction mixture changed from pale yellow to dark red. The solution was stripped of solvents, dissolved in CH_2Cl_2 and silica gel was added. Upon removal of the solvent under reduced pressure the coated silica gel was loaded on the top of a silica gel column packed in dry *n*-hexane. A first yellow band containing a mixture of unreacted $PhCH_2Mn(CO)_5$ and $Mn_2(CO)_{10}$ was eluted with pure *n*-hexane. A second red-colored band containing **1a** (79 mg, 4% yield) was eluted with a 1:9 mixture of CH_2Cl_2 and *n*-hexane. A third brown yellow-colored band containing **1c** (422 mg, 16%) was eluted with the same solvent mixture.

3.3. Manganation of *1* in a mixture of *n*-hexane and benzene

A solution of ligand **1** (1 g, 3 mmol) and $PhCH_2Mn(CO)_5$ (2.6 g, 9.1 mmol) in a 2:1 mixture of *n*-hexane (10 mL) and benzene (5 mL) was refluxed for 8 h under argon. The red colored solution was then evaporated under reduced pressure, the residue was dissolved in CH_2Cl_2 and silical gel was added. Upon removal of the solvent under reduced pressure the

coated silica was loaded on the top of SiO_2 column packed in dry *n*-hexane at 2 °C. Compound **1b** was eluted as a red colored band with a 1:4 mixture of CH_2Cl_2 and *n*-hexane and isolated upon removal of solvents and recrystallization from *n*-hexane as a red powder (770.5 mg, 51%).

3.4. Manganation of 2,3-diphenylbenzoquinoxaline *1* in toluene

A solution of ligand **1** (1 g, 3 mmol) and $PhCH_2$-$Mn(CO)_5$ (2.0 g, 7 mmol) in dry toluene (15 mL) was refluxed for 14 h under argon. The red colored solution was then evaporated under reduced pressure, the residue was dissolved in CH_2Cl_2 and silica gel was added. Upon removal of the solvent under reduced pressure the coated silica was loaded on the top of SiO_2column packed in dry *n*-hexane at 2 °C. A first yellow band containing $Mn_2(CO)_{10}$ (330 mg, 28%) was first eluted with a 1:4 mixture of CH_2Cl_2 and *n*-hexane. Compound **1a** was eluted a deep red band with a 1:1 mixture of CH_2Cl_2 and *n*-hexane and recovered as a red powder upon removal of the solvents under reduced pressure (830 mg, 41%). Complex **1a** [17]: HR MS (FAB^+) Calc. for $C_{32}H_{14}N_2O_8Mn_2$: 663.951104. Found: 663.951108. IR (CH_2Cl_2) ν(CO): 2076, 1999, 1980, 1940 cm^{-1}. ^1H NMR($CDCl_3$) δ 9.11 (s, 2H, H_{bqx}), 8.23 (dd, 2H, H_{Ph}, $^3J = 8.0$, $^4J = 1.0$), 8.15 (dd, 2H, $H_{benzoquinoxaline}$, $^3J = 6.0$, $^4J = 3.0$), 7.95 (d, 2H, H_{Ph}, $^3J = 8.0$), 7.67 (dd, 2H, $H_{benzoquinoxaline}$, $^3J = 7.0$, $^4J = 3.0$), 7.29 (td, 2H, H_{Ph}, $^3J = 8.0$, $^4J = 2.0$), 7.03 (td, 2H, H_{Ph}, $^3J = 8.0$, $^4J = 1.0$). ^{13}C NMR ($CDCl_3$, 268 K) δ 220.7, 214.5, 212.7, 212.6, 182.3, 162.7, 149.5, 141.5, 138.4, 133.5, 132.2, 130.8, 128.5, 128.4, 125.6, 123.6. MS (FAB^+) *m/e* 664.8 $[M + H]^+$, 580.8 $[M - 3CO]^+$, 551.8 $[M - 4CO]^+$, 383.9 $[M - 8CO - Mn]^+$, 331.0 $[M + 2H - 8CO - 2Mn]^+$. Complex **1b** [18]: Anal. Calc. for $C_{28}H_{15}N_2MnO_4$: C, 67.48; H, 3.03; N, 5.62. Found: C, 67.41; H, 3.27; N, 5.48. IR (CH_2Cl_2) ν(CO): 2071 (w), 1994 (s), 1976 (vs), 1936 (vs) cm^{-1}. ^1H NMR ($CDCl_3$) δ 9.19 (s, 1H, $H_{benzoquinoxaline}$), 8.68 (s, 1H, $H_{benzoquinoxaline}$), 8.18 (m, 2H), 8.08 (d, 1H, $H_{benzoquinoxaline}$, $^3J = 9.0$), 7.76 (m, 2H), 7.67–7.50 (m, 5H), 7.23–7.16 (m, 2H), 6.82, (td, 1H, $^3J = 7.0$, $^4J = 1.0$). ^{13}C NMR ($CDCl_3$) δ 220.8 (MnCO), 214.4 (MnCO), 213.4 (MnCO), 181.5, 163.5, 153.5, 148.4, 141.4, 140.2, 139.3, 137.0, 134.1, 133.6, 132.0, 130.2, 129.9, 129.2 (2C), 129.0(2C), 128.7, 128.6, 128.1, 127.9, 127.4, 124.7, 123.1. Complex **1c** [19]: Anal. Calc. for $C_{46}H_{28}N_2Mn_2O_8$: C, 65.26; H, 3.33; N, 3.31. Found: C, 65.39; H, 3.66; N, 3.11%. IR (CH_2Cl_2) ν(CO) 2076, 1998, 1980, 1938 cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.06 (d, 2H, $H_{phenylene}$, $^3J = 7.5$), 7.95 (d, 2H, $H_{phenylene}$, $^3J = 8.0$), 7.42 (m, 2H, H_{qx}), 7.29 (m, 4H, $H_{qx+}H_{phenylene}$), 7.03 (t*, 2H, $H_{phenylene}$, $^3J = 8.0$), 6.86 (t*, 2H, H_{Ph}, $^3J = 7.5$), 6.64 (t*, 4H, H_{Ph}, $^3J = 7.7$), 5.68 (d, 4H, H_{Ph}, $^3J = 7.0$), 4.53 (t, 2H, H_{benzyl}, $^3J = 3.9$), 3.33 (dd, 2H, CH_2–Ph, $^2J = 13.3$, $^3J = 3.6$), 3.10 (dd, 2H, CH_2–Ph, $^2J = 13.3$, $^3J = 3.6$). ^{13}C NMR ($CDCl_3$) δ 220.8 (MnCO), 214.6 (MnCO), 213.2 (MnCO), 211.3 (MnCO), 176.3, 157.3, 150.1, 147.9, 141.2, 134.6, 134.1, 130.6, 130.0, 128.8, 127.83, 127.81, 127.7, 123.9, 47.9, 46.3.

3.5. Experimental procedure for the X-ray diffraction analysis of *1a* and *1c*

Acquisition and processing parameters are displayed in Table 1. Reflections were collected with a Nonius KappaCCD diffractometer using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods, they were refined against $|F|$ and for all pertaining computations, the Nonius OPENMOLEN package was used [20]. Hydrogen atoms were introduced as fixed contributors.

Acknowledgments

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Appendix A. Supplementary data

NMR spectra of compounds **1** and **1a**–**c**. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 277448 (**1a**) and 277449 (**1c**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK, fax: +44 1223 336 033, deposit@ccdc.cam.ac.uk or www: www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.07.077.

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[18] Tetracarbonyl[(2,3-diphenyl-κC$^{1'}$)(benzo[g]quinoxaline-κ*N*)]manganese(I).

[19] Bis(tetracarbonylmanganese(I))[5,10-*trans*-dibenzyl-5,10-dihydro-2,3-(diphenyl-κC$^{1'}$,κC$^{1''}$)benzo[g]quinoxaline-κ*N*,κ*N*′].

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