LETTER

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Pyrazolone-based nitrido complexes: synthesis and nitrogen transfer to alkenes

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The first examples of alkylpyrazolone based nitridomanganese(v) complexes are here reported. Styrene was used as a test substrate to study the complex's ability to transfer nitrogen in stoichiometric reactions. Preliminary trials yielded 75 to 91% of *N*-(2-hydroxy-2-phenylethyl)-2,2,2-trifluoroacetamide. An X-ray crystal structure for one of the nitrido complexes is also provided.

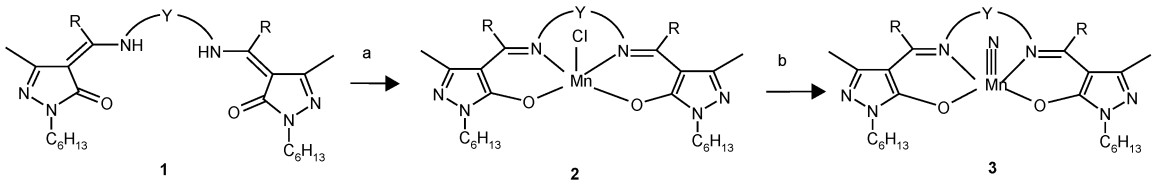
Oxidation of organic compounds by direct transfer of oxygen atoms using metal complexes catalysis has been the subject of numerous studies.[1] This procedure has become a very useful tool in both industrial and laboratory organic synthesis. Epoxidation and dihydroxylation of alkenes are very important examples[2] of these reactions. Nitrogen transfer, for instance metal-catalyzed amination of alkenes to obtain azyridines or aminoalcohols, is also well-known.[3] However, in these cases, expensive reagents are often required. Nitrogen transfer to olefins has also been achieved with nitridomanganese complexes, however, they are stoichiometric reagents and not catalysts. In one of the earlier reports, Groves and Takahashi[4] described cyclooctene aziridination using 5,10,15,20-(tetramesitylporphyrinate)manganese(v) and trifluoroacetic anhydride. Other procedures, using salen-based nitridomanganese complexes, allowed to obtain aziridines,[5,6] α-aminoketones,[7] 2-aminosugars,[8,9] aminoalcohols,[10] oxazolines[11,12] and sulfilimines.[13] Furthermore, different degrees of enantioselectivity have been accomplished using chiral imines. On the other hand, salen-type nitridomanganese complexes are easier to prepare than their porphyrine or phthalocyanine based homologs, and, consequently, they account for most of the advancements achieved to date.[7,10,14–18]

Pyrazolones are an important family of organic compounds[19] for theoretical and practical reasons.[20] They have been widely studied as a consequence of their numerous applications,[21–24] and in particular as chelating agents for solvent extraction of various elements.[25,26] Most pyrazolone derivatives so far reported bear an aryl ring at position 1, which usually diminishes their solubility. Schiff bases[27] and enamines[28] derived from pyrazolones are known but the same solubility problems may be expected. Therefore, their applications might be limited. To overcome this solubility problem, convenient syntheses of 1-*n*-alkyl derivatives of pyrazolones were reported a few years ago.[29] As expected, most of the products exhibited good solubility in regular solvents, (*i.e.*, acetone, ethanol, chloroform, ethyl acetate, ethyl ether, THF, toluene, ...), with crystallization becoming a lengthy procedure in some cases. Particularly, Schiff bases were prepared and it was found that they exist mainly as enamines.[30] The synthesis and characterization of nitridomanganese complexes using alkylpyrazolone derived enamines are reported in this paper, together with some preliminary results on their nitrogen transfer reactions.

The overall synthetic pathway is presented in Scheme 1. Enamines (**1**) were obtained as previously reported[31] and treated with $Mn(OAc)_3 \cdot H_2O$ and LiCl to obtain the Mn(III) chloro complexes **2**. Oxidation of **2** furnished the nitridomanganese complexes **3** in fairly good yields. Among several methods,[32] oxidation with NaClO in aqueous ammonia was chosen to prepare the nitrido complex because the reagents are cheap and readily available; indeed, ordinary bleach was used here.

Manganese(III) chloro complexes (**2**) were obtained as green flakes. They are paramagnetic as evidenced by magnetic susceptibility measurements. Fig. 1 shows a characteristic plot of the inverse of the magnetic susceptibility *versus* temperature for complexes **2**. Effective magnetic moments for **2a–c** were calculated from the slopes and equal to 4.4, 4.6 and 4.8 MB, respectively. These values are consistent with a d^4 electronic configuration with four unpaired electrons, which confirms the oxidation state of Mn. Far-IR spectra showed a band at 323 cm^{-1} that corresponds to the Mn–Cl bond stretching.[33]

Nitrido complexes (**3**) are air- and water-stable blue-violet flakes. Magnetic susceptibility values obtained for these compounds are negative and they do not depend on temperature, in the range from 100 to 300 K. It follows that nitridomanganese complexes **3** are diamagnetic. This behavior agrees with other reports on nitridomanganese complexes,[18] where the metal has an oxidation state of five with a low-spin d^2 electronic configuration. Far-IR spectra showed a band at 1043 cm^{-1} that corresponds to the Mn≡N bond stretching, being quite close to the reported[4,34] 1050 cm^{-1} for other nitrido complexes. Hydrogen atoms at the bridging carbons in complexes **3** are diastereotopic and they appear as multiplets between 3.3–3.7 ppm in the proton NMR spectra, in contrast with ligands **1** that exhibit one signal around 3.7 ppm,[30] without any splitting. In addition, the ligands[30] show a signal between 11–12 ppm that corresponds to N–H, not observed in the spectra of complexes **3**. An important signal in the ^{13}C NMR spectra of



a : 1. $Mn(OAc)_3.2H_2O$ - CH_3OH 2. LiCl b : 1.NH_4OH - CH_3OH/CH_2Cl_2 2. NaOCl

compound	R	Y
1a, 2a, 3a	CH_3	CH_2CH_2
1b, 2b, 3b	CH_3	$CH_2CH(CH_3)$
1c, 2c, 3c	CH_3CH_2	CH_2CH_2

Scheme 1 Synthesis of the nitridomanganese complexes **3**.

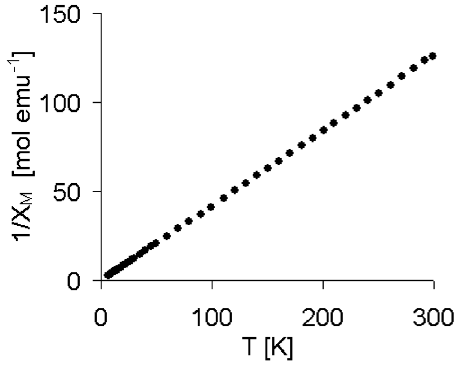


Fig. 1 Inverse molar magnetic susceptibility *versus* temperature (K) for compound **2a**.

nitrido complexes **3** appears at 170 ppm, which could correspond to the exocyclic C=N.

Single crystals were obtained for **3c** by slow evaporation of a methylene chloride–hexane solution. Efforts to obtain single crystals for **2a–c**, **3a** and **3b** were unsuccessful. A molecular diagram of **3c** is shown in Fig. 2 with the numbering scheme used. Table 1 presents selected bonds lengths and angles†.

The structure is monomeric and consists in a penta-coordinated Mn cation surrounded by a tetradentate ligand and a nitride anion. The ligand embraces the cation with its four coordinating atoms (N3A, N3B, O1A and O1B), defining the square base of an almost perfect square pyramidal environment. The apex, in turn, is occupied by the nitride N4, at a triple-bond distance of 1.502(3) Å. As stated above, the pyramidal geometry is nearly ideal, with a rather planar base [maximum deviation from the least squares basal plane is 0.006(1) Å]; Mn–$(O,N)_{basal}$ distances tightly distributed around the mean [1.935(32) Å] and an almost vertical apical axis [deviation of 3.2(1)°].

As a result of coordination, the structure presents a number of rings (five total), which extend in a rather planar fashion, the mean deviation for the 18 intervening atoms being less than 0.06(1) Å. The pendant hexyl groups, in turn, evolve almost perpendicular to the core in the same direction as the nitride apex, their longest C9···C14 axis subtending an angle of *ca.* 85(1)° to the core mean plane.

The **1c** ligand, which in the free state presents a clear enamine-ketone structure ($\nu_{C=O}$ 1619 cm^{-1}, ^{13}C NMR 169.7 ppm), seems to shift towards a state with a marked imino character when complexed. This is evidenced by both spectroscopic data (*viz.*, the loss of the C=O vibration at 1619 cm^{-1} and the appearance of a band at 1585 cm^{-1} corresponding to a C=N stretching mode), as well as by the change in the distribution of bond lengths. The most similar free ligands to **3c** reported so far and identified as enamino ketones are 1-(*n*-hexyl)-3-methyl-4-[1-(phenylamino)propylidene]-2-pyrazolin-5-one and *N*,*N*′-bis{1-[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-yl]ethyliden-1-yl}-1,6-diaminohexane. Their structures were recently reported[35] and selected bond distances are compared to **3c** in Fig. 3 (upper pair and lower pair of numbers, respectively). The trend of the bond length shifts in the chain N3–C5–C2–C1–O1 clearly points to the imino character of **3c**.

Monomeric units are related to each other through the [1 − *x*, 1 − *y*, 1 − *z*] symmetry operation at the cell center and parallel to each other at some 3.60(2) Å distance apart (Fig. 4). The resulting intercationic distance is 4.467(1) Å. Both pyramidal coordination polyhedra arrange such that the "concave" bases face each other and the nitride anions point outwards. The dimeric units, in turn, pack in a rather loose way, without any significant inter-dimeric interactions, short of the usual van der Waal's.

Styrene was used as a model olefin to test the nitrogen-transfer ability of compounds **3** (Scheme 2). As previously stated, this reaction is not catalytic, but a stoichiometric one. In a typical run, equimolar amounts of trifluoroacetic anhydride and **3** and a small excess of styrene were dissolved in

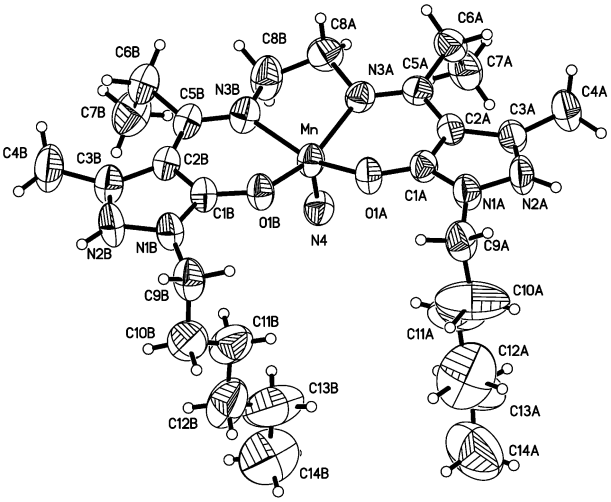


Fig. 2 Molecular diagram of compound **3c** showing the numbering scheme used. Displacement ellipsoids drawn at the 50% probability level.

† CCDC reference number 248574. See http://www.rsc.org/suppdata/nj/b4/b415101a/ for crystallographic data in .cif or other electronic format.

Table 1 Selected bond lengths (Å) and angles (°) for compound **3c**

Mn–O(1B)	1.900(2)	Mn–N(3A)	1.964(3)
Mn–O(1A)	1.909(2)	Mn–N(3B)	1.968(3)
Mn–N(4)	1.502(3)		
O(1A)–C(1A)	1.286(4)	O(1B)–C(1B)	1.289(4)
N(1A)–C(1A)	1.337(4)	N(1B)–C(1B)	1.340(4)
N(1A)–N(2A)	1.369(4)	N(1B)–N(2B)	1.367(4)
N(2A)–C(3A)	1.301(4)	N(2B)–C(3B)	1.305(5)
N(3A)–C(5A)	1.308(4)	N(3B)–C(5B)	1.309(4)
C(1A)–C(2A)	1.402(4)	C(1B)–C(2B)	1.399(5)
C(2A)–C(5A)	1.410(4)	C(2B)–C(5B)	1.405(5)
C(2A)–C(3A)	1.422(5)	C(2B)–C(3B)	1.416(5)
N(4)–Mn–O(1B)	106.82(15)	O(1A)–Mn–N(3A)	91.14(11)
N(4)–Mn–O(1A)	105.77(16)	N(4)–Mn–N(3B)	101.22(16)
O(1B)–Mn–O(1A)	80.41(10)	O(1B)–Mn–N(3B)	91.45(12)
N(4)–Mn–N(3A)	101.03(15)	O(1A)–Mn–N(3B)	153.01(13)
O(1B)–Mn–N(3A)	152.14(13)	N(3A)–Mn–N(3B)	84.15(14)

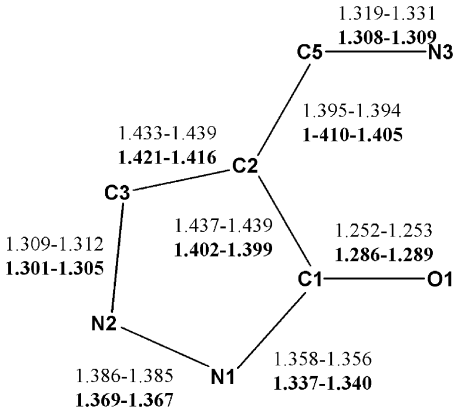


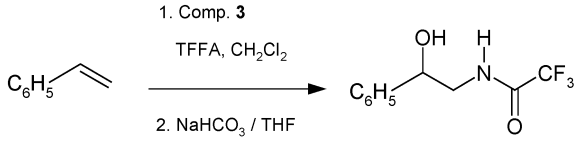
Fig. 3 Comparison between selected bond distances for **3c** (bold type) and related free ligands[36] (regular type).

methylene chloride. The solution was stirred for 1 h at room temperature and then neutralized. The organic phase was analyzed by GC-MS, the yields of *N*-(2-hydroxy-2-phenylethyl)-2,2,2-trifluoroacetamide were estimated by comparing with a standard of the expected product that was synthesized as reported.[36] Complexes **3a**, **3b** and **3c** furnished the desired amide in 91, 75 and 77% yields, respectively.

Experimental

Materials and methods

Chemicals were purchased from Merck, Sigma, Aldrich and J. T. Baker. The ligands *N*,*N*′-bis[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-ylethyliden-1-yl]ethylenediamine (**1a**), *N*,*N*′-bis[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-ylethyliden-1-yl]-1,2-diaminopropane (**1b**) and *N*,*N*′-bis[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-ylpropyliden-1-yl]ethylenediamine (**1c**) were prepared according to procedures described in the literature.[31]



Scheme 2 Conversion of styrene to *N*-(2-hydroxy-2-phenylethyl)-2,2,2-trifluoroacetamide with nitridomanganese complexes **3**.

Compounds were characterized by FTIR (Nicolet Magna 550), ^{13}C and ^{1}H NMR (Bruker AC 250P, 62.9 and 250 MHz, respectively, TMS as internal standard and deuterated chloroform as solvent, operating temperature 28 °C) spectroscopies. ^{13}C-^{1}H correlation and DEPT spectra were also used to assign the signals. The numbering used for signal assignment is shown in Fig. 5. Melting points were obtained on a Kofler microscope and are uncorrected. Elemental analyses for C, H, N (Fisons EA 1108), Cl (Euroglas ECS 1000 microcoulombimeter) and Mn (acid digestion and plasma analysis, GBG ICP spectrophotometer) were also performed.

The magnetic susceptibility (SHE-VTS 906 SQUID susceptometer) was measured between 6 K and 300 K, under an applied field of 2 kOe (0.2 Tesla). Powder samples were placed and compacted inside a gelatine capsule. The temperature-independent magnetic contribution due to the sample holder was subtracted at all temperatures. Measurements were performed in the zero-field-cooled (ZFC) mode, that is, cooling the sample under zero field and then warming it under the given applied magnetic field. The diamagnetic contribution due to the core electrons was estimated using Pascal constants and subtracted from the experimental values.

Synthesis of chloromanganese(III) complexes (2). General procedure

To a solution of ligand **1** (8.0 mmol) in CH_3OH (30 ml) solid $Mn(OAc)_3 \cdot 2H_2O$ (2.41 g, 9.0 mmol) was added in one portion. The resulting solution was heated at reflux for 1 h. Solid LiCl (1.15 g, 27.0 mmol) was then added and the mixture was heated at reflux for an additional 0.5 h. The solution volume was reduced to 50% by evaporation and the residue was left to stand overnight. The green solid was filtered off and crystallized from a 90 : 10 ethanol–water mixture.

Chloro-*N*,*N*′-bis{1-[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-yl]ethyliden-1-yl}ethylenediaminomanganese(III)·4H_2O (2a). Yield 98%; mp 138 °C. IR (KBr) ν/cm^{-1}: 3297 (OH), 1575 (C=N), 603 (Mn–N), 478 (Mn–O), 324 (Mn–Cl). Anal. calcd for $C_{26}H_{50}N_6O_6MnCl$: C, 49.30; H, 7.96; N, 13.27; Cl, 5.60; Mn, 8.68; found: C, 49.70; H, 8.10; N, 13.30; Cl, 5.30; Mn, 8.30.

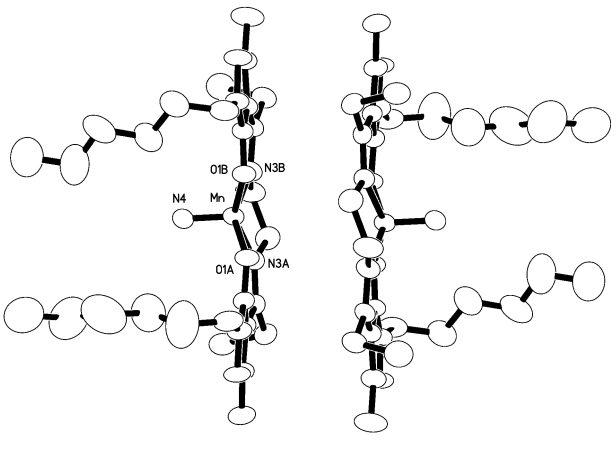


Fig. 4 Dinuclear unit in compound **3c** built up around the symmetry center at [1 − *x*, 1 − *y*, 1 − *z*].

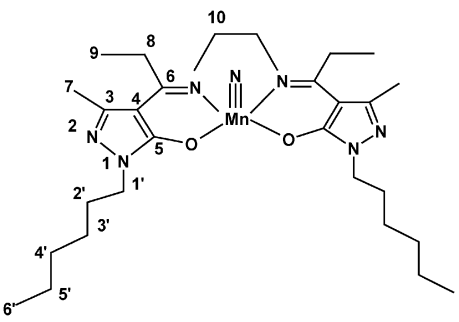


Fig. 5 Numbering used for NMR signal assignment.

Chloro-*N,N'*-bis{1-[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-yl]}ethyliden-1-yl}-1,2-diaminopropanemanganese(III)·H_2O (2b). Yield 91%; mp 55 °C. IR (KBr) ν/cm^{-1}: 3300 (OH), 1572 (C=N), 602 (Mn–N), 470 (Mn–O), 323 (Mn–Cl). Anal. calcd for $C_{27}H_{46}N_6O_3MnCl$: C, 54.68; H, 7.82; N, 14.20; Cl, 5.98; Mn, 9.26. Found: C, 54.90; H, 7.90; N, 13.80; Cl, 5.60; Mn, 8.98.

Chloro–*N,N'*-bis{1-[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-yl]propyliden-1-yl}ethylenediaminomanganese(III)·$2H_2O$ (2c). Yield 80%; mp 87 °C. IR (KBr) ν/cm^{-1}: 3250 (OH), 1575 (C=N), 604 (Mn–N), 478 (Mn–O), 323 (Mn–Cl). Anal. calcd for $C_{28}H_{50}N_6O_4MnCl$: C, 53.80; H, 8.10; N, 13.40; Cl, 5.70; Mn, 8.80; found: C, 54.00; H, 8.10; N, 13.30; Cl, 5.70; Mn, 8.60.

Synthesis of nitridomanganese(V) complexes (3). General procedure

To a solution of complex **2** (0.50 mmol) in a CH_2Cl_2–CH_3OH mixture (4 : 1, 50 ml) aqueous ammonia was added in one portion (1.0 ml 25%, 7.0 mmol). The mixture was stirred vigorously for 10 min and then bleach (3.3 ml 5.5% NaClO, 2.3 mmol) was added dropwise. The resulting biphasic mixture was stirred at room temperature until its color changed to blue-violet. The product was extracted with methylene chloride, then washed with water to neutral pH. The solution was then concentrated in a rotary evaporator and the remaining material was crystallized from a 90 : 10 ethanol–water mixture.

Nitrido-*N,N'*-bis{1-[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-yl]ethyliden-1-yl}ethylenediaminomanganese(V) (3a). Yield 72%; mp 126 °C. ^{1}H NMR δ: 0.88 (t, 6 H, J = 6.3 Hz, 2 CH_3-6′), 1.32 (m, 12 H, 2 CH_2-3′, 2 CH_2-4′ and 2 CH_2-5′), 1.76 (m, 4 H, 2 CH_2-2′), 2.34, 2.39 (both s, 12 H, 4 CH_3), 3.31 (m, 2 H, CH_2), 3.71 (m, 2 H, CH_2), 3.82 (t, 4 H, J = 7.4 Hz, 2 CH_2-1′). ^{13}C NMR δ: 13.90 (2 C-6′), 17.26, 17.65 (2 C-7, 2 C-8), 22.50, 26.30, 29.20, 31.30 (2 C-5′, 2 C-4′, 2 C-2′, 2 C-3′), 45.02 (2 C-1′), 54.92 (2 C-9), 103.50 (2 C-4), 144.82 (2 C-3), 162.04 (2 C-5), 169.17 (2 C=N C-6). IR (KBr) ν/cm^{-1}: 1583 (C=N), 1043 (Mn≡N), 607 (Mn–N), 474 (Mn–O). Anal. calcd for $C_{26}H_{42}N_7O_2Mn$: C, 57.87; H, 7.85; N, 18.17; Mn, 10.18; found: C, 58.10; H, 7.80; N, 18.20; Mn, 10.20.

Nitrido-*N,N'*-bis{1-[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-yl]ethyliden-1-yl}-1,2-diaminopropanemanganese(V) (3b). Yield 69%; mp 40 °C. ^{1}H NMR δ: 0.81 (t, 6 H, J = 6.0 Hz, 2 CH_3-6′), 1.31 (m, 12 H, 2 CH_2-3′, 2 CH_2-4′ and 2 CH_2-5′), 1.37 (d, 3 H, J = 6.5 Hz, CH_3), 1.65 (m, 4 H, 2 CH_2-2′), 2.21, 2.29 (both s, 12 H, 4 CH_3), 3.50 (m, 1 H, CH_2), 3.67 (m, 1 H, CH_2), 3.73 (m, 4 H, 2 CH_2-1′), 3.96 (m, 1 H, CH). ^{13}C NMR δ: 13.97 (2 C-6′), 15.42 (2 C-8), 17.26 (2 C-7), 19.40 (C-10), 22.50, 26.32, 29.00, 31.31 (2 C-5′, 2 C-4′, 2 C-2′, 2 C-3′), 45.04 (2 C-1′), 49.50, 49.80 (2 C-9), 104.00 (2 C-4), 145.00 (2 C-3), 164.30 (2 C-5); 168.4, 169.10 (2 C=N C-6). IR (KBr) ν/cm^{-1}: 1583 (C=N), 1048 (Mn≡N), 601 (Mn–N), 485 (Mn–O). Anal. calcd for $C_{27}H_{44}N_7O_2Mn$: C, 58.58; H, 8.01; N, 17.71; Mn, 9.92; found: C, 58.98; H, 8.10; N, 17.50; Mn, 9.60.

Nitrido-*N,N'*-bis{1-[1-(*n*-hexyl)-3-methyl-5-oxo-2-pyrazolin-4-yl]propyliden-1-yl}ethylenediaminomanganese(V) (3c). Yield 67%; mp 105 °C. ^{1}H NMR δ: 0.80 (t, 6 H, J = 6.2 Hz, 2 CH_3-6′), 1.12 (t, 6 H, J = 7.6 Hz, 2 CH_3), 1.25 (m, 12 H, 2 CH_2-3′, 2 CH_2-4′ and 2 CH_2-5′), 1.69 (m, 4 H, 2 CH_2-2′), 2.28 (s, 6 H, 2 CH_3), 2.72 (q, 4 H, J = 7.6 Hz, 2 CH_2), 3.34 (m, 2 H, CH_2), 3.61 (m, 2 H, CH_2), 3.74 (t, 4 H, J = 7.4 Hz, 2 CH_2-1′). ^{13}C NMR δ: 11.81 (2 C-9), 13.94 (2 C-6′), 16.62 (2 C-7), 22.46 (2 C-5′), 23.34 (2 C-8), 26.31, 28.88, 31.28 (2 C-4′, 2 C-2′, 2 C-3′), 45.07 (2 C-1′), 54.24 (2 C-10), 102.18 (2 C-4), 144.38 (2 C-3), 162.49 (2 C-5), 173.83 (2 C=N C-6). IR (KBr) ν/cm^{-1}: 1585 (C=N), 1043 (Mn≡N), 606 (Mn–N), 473 (Mn–O). Anal. calcd for $C_{28}H_{46}N_7O_2Mn$: C, 59.25; H, 8.17; N, 17.27; Mn, 9.68; found: C, 59.60; H, 8.20; N, 17.30; Mn, 9.72.

Nitrogen transfer reactions

Styrene (0.04 mmol, 0.05 ml) and trifluoroacetic anhydride (0.36 mmol, 0.05 ml) were dissolved in methylene chloride (15 ml) and then **3** (0.36 mmol) was added at once. The solution was stirred for 1 h and then neutralized by adding a mixture of aqueous saturated $NaHCO_3$ (5 ml) and THF (5 ml). The organic phase was analyzed by GC-MS (Hewlett Packard HP-5890 series 2 gas chromatograph and HP 5972 mass spectrometer). Yields of *N*-(2-hydroxy-2-phenylethyl)-2,2,2-trifluoroacetamide were 91, 75 and 77% when **3a**, **3b** and **3c** were used, respectively.

X-Ray crystallography

A blue-violet single crystal with dimensions of 0.25 × 0.24 × 0.13 mm^3 was mounted on a Bruker SMART CCD area-detector diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å). A total of 9221 reflections were collected in the range 1.78° ≤ θ ≤ 27.99° at 297 K, 6483 of which were independent (R_{int} = 0.062) and 3338 observed with [$I > 2\sigma(I)$]. The structure was solved by direct methods (SHELXS97) and successive difference Fourier syntheses, and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located theoretically and refined with a riding model, both in position as well as in isotropic thermal parameters (SHELXL97). Crystal data for **3c**: $C_{28}H_{48}MnN_7O_2$, MW 569.67, triclinic, space group P-1, a = 9.2780(11), b = 13.5310(16), c = 13.9489(17) Å, α = 113.953(3)°, β = 90.227(2)°, γ = 102.320(2)°, U = 1555.4(3) Å^3, Z = 2, D_c = 1.216 g cm^{-3}, final R_1 = 0.0672 and wR_2 = 0.1961 [$I > 2\sigma(I)$].

Acknowledgements

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