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(Di)Triazolylidene Manganese Complexes in Catalytic Oxidation of Alcohols to Ketones and Aldehydes

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Carbonyl manganese complexes with chelating or bridging mesoionic di(1,2,3-triazolylidene) ligands were efficiently synthesised and fully characterised, including the X-ray diffraction study of a bimetallic manganese(0) complex. This unprecedented bimetallic complex displayed high yield and selectivity in the catalytic oxidation of secondary alcohols and benzyl alcohol with *tert*-butyl hydroperoxide under mild conditions.

Manganese complexes have emerged in the last few years as excellent catalysts for numerous transformations.¹ The vast natural abundance of manganese—it is the third most abundant metal in Earth's crust—together with its low price and non-toxicity render it a particularly attractive alternative to expensive noble metals in catalysis. Moreover, manganese offers facile access to multiple oxidation states, and it can accommodate up to seven ligands in its first coordination sphere, hence providing a large window of reactivity. Recent work of Beller,² Kempe,³ Milstein,⁴ Kirchner,⁵ Trovitch,^{1b,6} Turculet,⁷ and other groups⁸ have demonstrated the great potential of manganese complexes in hydrogenation, hydrosilylation, and hydrogen transfer processes. Manganese-catalysed oxidation reactions have mainly focussed on alkene epoxidation and bio-inspired C-H functionalisations with coordination compounds featuring nitrogen- and oxygen-based ligands.^{9,1b} More recently, alcohol dehydrogenation has been demonstrated with manganese-based catalysts, though the carbonyl products were either directly trapped for oxidative coupling reactions,^{2–8} or further oxidized. Only very few Mn complexes are known to catalyse the oxidation of alcohols,^{10,11} and the selective formation of aldehydes is still a challenge.^{11c}

We hypothesized that selective alcohol oxidation with manganese may be imparted by mesoionic 1,2,3-triazolylidene (trz) ligands, a subclass of N-heterocyclic carbenes (NHCs),¹² which offer attractive opportunities for oxidation catalysis. They can act as electron reservoirs in redox transformations,¹³ and additionally, their strong σ -donor capability may facilitate the stabilisation of high oxidation states in transition metals. In comparison with noble metals, the synthesis of 1,2,3-triazolylidene complexes of first-row transition metals and their application in catalysis have been scarcely studied.^{14,15} Noteworthy is the application of well-defined triazolylidene copper complexes in catalytic [3+2] cycloaddition between azides and alkynes.¹⁶ The only other examples in base-metal catalysis with triazolylidene ligands are limited to the electrocatalytic production of hydrogen mediated by a trz Co complex,¹⁷ and the recent examples reported by some of us using Fe¹⁸ and Ni¹⁹ complexes in hydrosilylation and C-C bond formation reactions.

Recently, we disclosed the first purely organometallic *fac*-[Mn(bis-NHC^R)(CO)₃Br] (R = methyl, mesityl) complexes with unprecedented activity for the selective electrocatalytic reduction of CO₂ to CO,²⁰ and demonstrated the efficiency of these complexes in the reduction of carbonyl groups through hydrosilylation reactions.^{8c} One of the most interesting features of this new type of complexes is their air and moisture stability, which allows catalytic experiments to be performed in an open flask. Encouraged by these results, we have now investigated the coordination chemistry of di(1,2,3-triazolylidenes) to manganese and evaluated the performance of the new complexes in catalysis.

The monometallic manganese(I) complex [Mn(CO)₃(di-trz)Br] (**2**) containing a bidentate chelating di(triazolylidene) ligand was prepared in 48% yield from ditriazolium triflate salt **1a**,^{12d} which was subjected to anion exchange for bromide followed by treatment with Mn(CO)₅Br in the presence of 2 equiv. of KOBu^t (Scheme 1). Surprisingly, when the same reaction protocol was applied to the ditriazolium triflate salt **1b**^{12e} bearing an ethyl group on N1 rather than the mesityl group as in **1a**, the

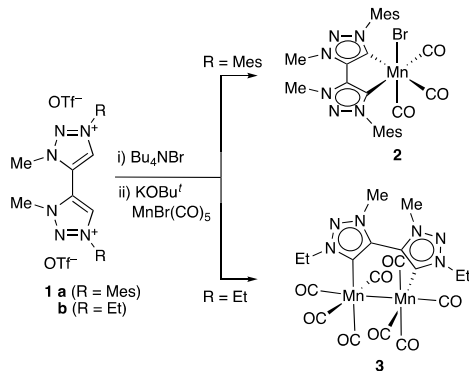
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bimetallic manganese(0) complex $[\text{Mn}_2(\text{CO})_8(\mu\text{-di-trz})]$ (**3**) with the two metal centers bridged by the di(triazolylidene) ligand was isolated from the reaction in 52% yield with indication of concomitant bromine formation. Both complexes **2** and **3** are air- and moisture-stable at ambient temperature and were fully characterised using NMR and FTIR spectroscopy, elemental analysis, and in the case of **3** by X-ray crystallography.



Scheme 1 Synthesis of manganese complexes **2** and **3** (Mes = 2,4,6-trimethylphenyl; Et = ethyl).

The molecular structure of complex **3** (Fig. 1)[†] features two formally zero-valent Mn centers in a slightly distorted octahedral geometry with a Mn–Mn bond length of 2.9389(4) Å, comparable to the distance observed in $\text{Mn}_2(\text{CO})_{10}$,²¹ and consistent with the presence of a formal single bond required to account for the favored 18-electron configuration of both manganese centers. The Mn–C_{trz} bond length in **3** is 2.044(15) Å, comparable to that observed in tris(trz)borate–Mn(CO)₃ the only example of a triazolylidene manganese complex reported in the literature.¹⁵



Figure 1 X-ray crystal structure of **3**. Hydrogen atoms are omitted for clarity; selected bond lengths: Mn1–Mn1a 2.9389(4) Å, Mn1–C1 2.0440(15) Å.

The spectroscopic features of **3** are consistent with the crystallographically determined structure. The (di)triazolylidene ligand displays a single set of resonances, as expected for a highly symmetric complex, with a resonance at 4.15 ppm for the N–CH₃ protons and a set of resonances for the ethyl wingtip group at 4.77 and 1.63 ppm. The Mn–C_{trz} resonance is observed at 181.2 ppm in the ¹³C NMR spectrum. The carbonyl ligands in **3** give rise to three strong IR bands at 1971, 1912 and 1881 cm⁻¹ and a relatively weak band at 2035 cm⁻¹, in accordance with

reported data for C₂-symmetric tetracarbonyl dimers of Mn.²² In contrast, the IR spectrum of **2** showed the expected pattern for a *fac*-tricarbonyl species with three bands corresponding to the CO stretching frequencies at 2005, 1918, and 1884 cm⁻¹, at lower wavelengths than those reported for the imidazole-2-ylidene analogue *fac*-[Mn(bis-NHC^{Mes})(CO)₃Br] (2007, 1923, and 1887 cm⁻¹), indicating stronger donor properties of the triazolylidene vs imidazole-2-ylidene ligand.^{8c} The carbenic carbon of the Mn(I) complex **2** resonates at lower field than that in the Mn(0) complex **3** (δ_{C} 196.3 vs 181.2 ppm), as expected for a higher metal oxidation state.

The new complexes **2** and **3** were evaluated as catalyst precursors for the oxidation of selected alcohols with *tert*-butyl hydroperoxide (TBHP) as oxidant. First, the reaction conditions were optimised using 1-phenylethanol as a model substrate and complex **3** as catalyst (Table 1). Initially, the reaction was carried out in MeCN at 80 °C with a catalyst loading of 1 mol% and using TBHP in slight excess (1:1.5 ratio of substrate/oxidant). Under these conditions **3** induced quantitative conversion of 1-phenylethanol to acetophenone in 2 h (Table 1, entry 1). Similar conversion rates were obtained when the reaction temperature was gradually decreased to 60 °C and 40 °C (entries 2, 3, Fig. S7). At 25 °C the reaction is slower, achieving 82% yield in 24 h (entries 4, 5). Lower catalytic activity was observed when MeCN was replaced by CH₂Cl₂ or CHCl₃, or when the oxidation was run under neat conditions (entries 6–11, Fig. S8). Decreasing the catalyst loading to 0.5 mol% led to a marked drop in activity, irrespective whether the catalyst quantity is reduced or the substrate/oxidant concentration is increased (45% conversion within 24–48 h; entries 12, 13, Fig. S9). Longer reaction times are needed (6 h) to achieve completion of the reaction when the amount of TBHP is reduced to 1 equivalent (Fig. S10). When the sacrificial oxidant was changed from TBHP to aqueous H₂O₂ (1.5 equiv.), only 27% of acetophenone was produced after 24 h, suggesting a critical role of the oxidant.

Table 1 Oxidation of 1-phenylethanol with complex **3**^a

Entry	Solvent	T (°C)	t (h)	Yield (%) ^b
1	MeCN	80	2	≥99
2	MeCN	60	2	≥99
3	MeCN	40	2	≥99
4	MeCN	25	2	14
5	MeCN	25	24	82
6	CH ₂ Cl ₂	40	2	19
7	CH ₂ Cl ₂	40	24	≥99
8	CHCl ₃	40	2	55
9	CHCl ₃	40	24	≥99
10	neat	40	2	61
11	neat	40	8	≥99
12 ^c	MeCN	40	24	45
13 ^c	MeCN	40	48	45

^a Reaction conditions: 1-phenylethanol (0.5 mmol), catalyst **3** (1 mol%), TBHP (0.75 mmol), mesitylene (0.5 mmol), solvent (0.4 mL); ^b Determined by ¹H NMR spectroscopy using mesitylene as internal standard. ^c Reactions performed with 0.5 mol% complex **3**.

To assess the impact of the triazolylidene ligand, we compared the catalytic performance of complexes **2** and **3** to that of the related bis-imidazolylidene complex *fac*-[Mn(CO)₃(bis-NHC^{Me})Br] (**4**),²⁰ and to Mn₂(CO)₁₀ (**5**) under optimised reaction conditions (MeCN, 40 °C, 1 mol% catalyst; Fig. 2). The pertinent

time-conversion profiles indicate that complex **3** is considerably more active than the other manganese compounds. The selective conversion of 1-phenylethanol to acetophenone was completed in 2 h with a turnover frequency $\text{TOF}_{\text{ini}} = 72 \text{ h}^{-1}$ (measured at 15 min of reaction, TOF_{50} at 50% conversion is 56 h^{-1}), while complexes **2** and **4** featured three times lower activity ($\text{TOF}_{\text{ini}} < 24 \text{ h}^{-1}$) and reached a mere 22% and 16% yield, respectively, in the time span that complex **3** accomplished quantitative conversion (2h). No induction period was observed, indicating that the catalytically active species is formed rapidly upon addition of the oxidant to the reaction medium. Interestingly, the introduction of the triazolylidene ligand in the coordination sphere of the manganese(0) center has a markedly positive effect and enhanced the catalytic activity compared to the carbene-free dimer $\text{Mn}_2(\text{CO})_{10}$ (cf activity of complex **3** vs **5**).

Electrochemical analysis of complexes **2–5** offers some hints for the high catalytic activity of complex **3** in alcohol oxidation. Complexes **2–4** all show quasi-reversible oxidation at high scan rate and an *EC* mechanism at lower scan rate. While the manganese(I) complexes **2** and **4** are reversibly oxidised at similar potential ($E_{1/2} = +0.30$ and $+0.39 \text{ V}$, respectively), the manganese(0) system is much easier to oxidise with $E_{1/2} = -0.02 \text{ V}$ (all potentials vs Fc/Fc^+ in MeCN). Complex **5** features an irreversible oxidation at $E_{\text{pa}} = +0.94 \text{ V}$. The facile oxidation of complex **3** may therefore be critical for fast turnover.

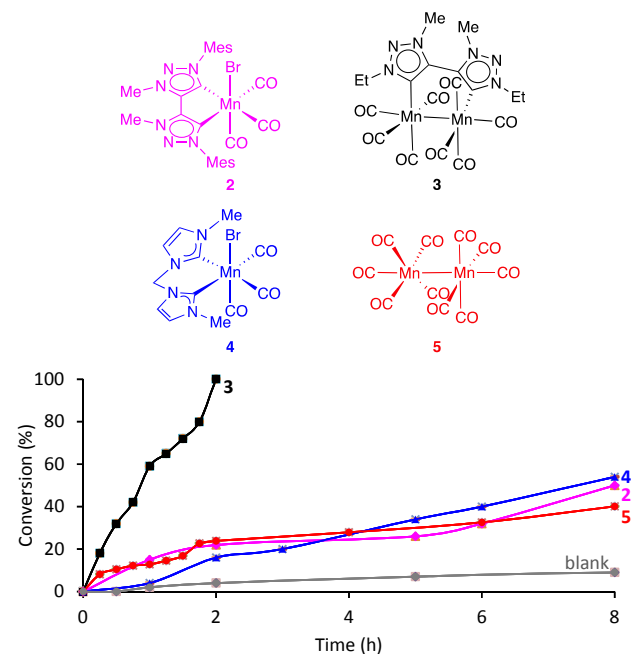


Figure 2 Kinetic profiles of complexes **2–5** in the oxidation of 1-phenylethanol with TBHP in MeCN at 40 °C.

To explore the scope of **3** as catalyst, we studied the oxidation of a variety of alcohols with TBHP under the optimised conditions (1 mol% catalyst, MeCN, 40 °C; Table 2). Secondary aromatic as well as both cyclic and linear aliphatic alcohols were efficiently oxidised to the corresponding ketones with good to moderate yields (72–99%, Table 2). Benzyl alcohol was

selectively oxidised to benzaldehyde (84%, Table 2) in high yield and **very good** selectivity with only minor overoxidation (<7%) to the corresponding acid. However, primary aliphatic alcohols such as 2-phenylethanol are not oxidised under the same reaction conditions. As far as we know, this work represents the first example of oxidation of alcohols catalysed by triazolylidene complexes of first-row transition metals,^{12c} and the most active Mn-based catalyst for oxidation of alcohols with TBHP under mild conditions (Tables S1, S2).^{10,11} Oxidation of selected secondary benzyl alcohols with TBHP has been successfully achieved by related trz ruthenium complexes containing a pyridyl or picolyl functionality. However, these catalytic systems were inactive towards aliphatic secondary alcohols and primary benzyl alcohols were overoxidised.^{13,23} Iron(II) complexes bearing NHC and bipyridyl ligands efficiently catalyse the oxidation of 1-phenylethanol with TBHP, however longer reaction times, higher temperature, and higher catalyst loadings were needed to achieve quantitative conversion.²⁴

Table 2 Oxidation of alcohols with complex **3**^a

Entry	Substrate	Product	t (h)	Yield (%) ^b
1	1-Phenylethanol	Acetophenone	2	≥99 (80)
2	Cyclohexanol	Cyclohexanone	8	97 (92)
3	1,2,3,4-Tetrahydro-1-naphthol	1-Tetralone	8	84 ^c
4	1-Phenyl-1-propanol	Propiophenone	8	96 ^c (67)
5 ^d	2-Hexanol	2-Hexanone	24	77 (73)
6	1-Cyclopropylethanol	Cyclopropyl methyl ketone	24	72 (65)
7	Benzyl alcohol	Benzaldehyde	8	84 (81)
8 ^d	2-Phenylethanol	---	24	0

^aReaction conditions: alcohol (0.5 mmol), catalyst **3** (1 mol%), TBHP (0.75 mmol), mesitylene (0.5 mmol), acetonitrile (0.4 mL) at 40 °C; ^bYields determined by ¹H NMR spectroscopy using mesitylene as internal standard. In parenthesis are isolated yields. ^cConversion calculated by GC using n-tetradecane as internal standard. ^dReaction performed with 2 mol% of **3**.

To probe the longevity of complex **3** and its potential for reuse, multiple fresh batches of substrate (1-phenylethanol) and oxidant were sequentially added to the reaction mixture. The catalyst was reused for up to 6 cycles without any loss of selectivity and quantitative yields of acetophenone were observed after each run, providing an accumulated turnover number $\text{TON} = 600$. While this productivity implies a high catalyst robustness, activity gradually erodes and the time to reach completion increases with every addition of fresh substrate from 2 h in the first cycle up to 24 h for the sixth cycle (Fig. S11).

Mechanistic insights have been obtained by poisoning experiments and *in operando* spectroscopy. Catalyst homogeneity was assessed by the mercury drop test experiment to distinguish between homogeneous and heterogeneous catalysts, since mercury leads to the amalgamation of the surface of a heterogeneous catalyst.²⁵ Performing the oxidation of 1-phenylethanol with **3** (1 mol%) in the presence of a large excess of $\text{Hg}(0)$ (>1000 equiv.) did not affect the conversion. Similar conversion profiles were obtained for catalytic runs in the presence and absence of mercury, indicating that the catalytic species derived from complex **3** remains homogeneous (Fig. S12). Reaction monitoring *in operando* by IR spectroscopy reveals an increase of the characteristic carbonyl intensity at 1688 cm^{-1} of the

acetophenone product, which correlates with conversions determined from ^1H NMR samples. A substoichiometric run (complex **3**/phenylethanol/TBHP 1:4:4) reveals a rapid loss of the characteristic CO bands of complex **3** at 1971, 1912 and 1881 cm^{-1} , which supports manganese oxidation with concomitant loss of CO as a critical step for catalyst activation (cf electrochemistry).

In conclusion, we describe the synthesis of new Mn(0) and Mn(I) complexes containing 1,2,3-triazolyldiene ligands and their application in oxidation of alcohols to synthetically versatile carbonyl compounds. The catalytic process is remarkably selective and suppresses overoxidation, and is applicable to a variety of alcohols under mild conditions (40 °C). Further investigation of the application of the organometallic manganese complexes in oxidation and reduction reactions, and in elucidating the reaction mechanism is currently underway in our laboratories.

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Conflicts of interest

There are no conflicts to declare.

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