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N- vs *O*-Coordination in cyclomanganation of 1,5-diaryl-3-(2-pyridyl)pentane-1,5-diones and 3-(2-pyridyl)chalcones; cyclomanganation at saturated carbon and the crystal structure of [1,5-diphenyl-κC^2-3-(2-pyridyl-κ*N*) pentan-2-yl-κC^2-1,5-dione-κO^1κO^5] tetracarbonylmanganesetricarbonylmanganese

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Abstract

Reaction of 1,5-diphenyl-3-(2-pyridyl)pentane-1,5-dione (**5a**) with 2.5 moles of benzylpentacarbonylmanganese in petroleum spirit under reflux gives a small amount of the symmetric di-aryl-manganated product [1,5-diphenyl-κC^2-3-(2-pyridyl)pentane-1,5-dione-κO^1κO^5]bis-(tetracarbonylmanganese) (**7a**), but mostly [1,5-diphenyl-κC^2-3-(2-pyridyl-κ*N*)pentan-2-yl- κC^2-1,5-dione-κO^1κO^5]tetracarbonylmanganesetricarbonylmanganese (**6a**) which is manganated at only one aryl carbon [by $Mn(CO)_4$] but also [by $Mn(CO)_3$ with *N* and *O* coordination] at the methylene carbon adjacent to the $Mn(CO)_4$-coordinated ketone carbonyl. The latter is a rare example of direct cyclomanganation at a saturated carbon and the only known case adjacent to a carbonyl group; the X-ray crystal structure of **6a** is reported. With 3 moles of benzylpentacarbonylmanganese the yield of **6a** remains unchanged but some trimanganation product [1, 5-diphenyl-κ$C^{2'}$κ$C^{2'''}$-3-(2-pyridyl-κ*N*)pentan-2-yl-κC^2-1, 5-dione-κO^1κO^5]tris-(tetracarbonylmanganese) (**8a**) is formed, presumably from **7a**. Routes to products are proposed and activating factors considered. 1,5-Di-(2-thienyl)-3-(2-pyridyl)pentane-1,5-dione (**5b**) and its 3-thienyl isomer (**5c**) similarly give **6a** analogues [1,5-di-(2-thienyl-κC^3)-3-(2-pyridyl-κ*N*)pentan-2-yl-κC^2-1, 5-dione-κO^1κO^5]tetracarbonylmanganesetricarbonylmanganese (**6b**) and [1,5-di-(3-thienyl-κC^2)-3-(2-pyridyl-κ*N*)pentan-2-yl-κC^2-1,5-dione-κO^1κO^5]tetracarbonylmanganesetricarbonylmanganese (**6c**).

Also reported are the mono-cyclomanganation product [1-(2,6-dimethoxyphenyl)-3-(2-pyridyl-κ*N*)prop-2-en-2-yl-κC^2-1-one]tetracarbonylmanganese (**16**) and dicyclomanganation product [1-(2,5-dimethyl-3-thienyl-κC^4)-3-(2-pyridyl-κ*N*)prop-2-en-2-yl-κC^2-1-one-κ*O*]bis-(tetracarbonylmanganese) (**17**) from reaction of the respective (*E*)-1-aryl-3-(2-pyridyl)prop-2-en-1-ones (3-(2-pyridyl)chalcones), the first reported examples of enone metallation at the α-carbon via *N*-coordination by a β-2-pyridyl group.

Keywords: Manganese; Cyclometallation; Metallacycle; Crystal structure; Pyridyl; Chalcone

1. Introduction

We have reported on the competitive formation of *ortho*-aryl and β-alkenyl *O*-coordinated cyclomanganation products (e.g., **1** and **2**) of chalcones [(*E*)-1,3-diaryl-

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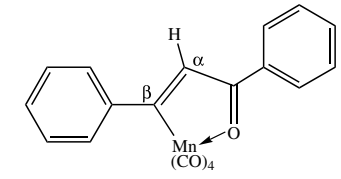
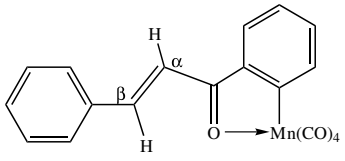
prop-2-en-1-ones] [1a]. For 1,5-diphenylpenta-1,4-dien-3-ones only β-manganation is available and derivatives of **3** are formed [1c]. Because of the rich vein of synthetic chemistry mined from coupling these compounds with unsaturated organic molecules [1b,1c], we became interested in extending study to molecules in which a nitrogen atom could compete for metal coordination with C=O leading to alternative manganation sites, e.g., for 3-(2-pyridyl)chalcones at the enone α-carbon to form **4** rather than at the enone β-carbon as in **1** or aryl carbon as in **2**; no such metallation (cf **4**) has previously been reported.

In applying standard base-catalysed condensation conditions to pyridine-2-carboxaldehyde and acetophenone in a 1:1 mole ratio to synthesise the 2-pyridylchalcone precursor of **4**, we rediscovered cf [2] the strong tendency for 2-pyridinecarboxaldehyde to react with two molecules of acetophenone leading instead to the symmetrical 1,5-diaryl-3-(2-pyridyl)pentane-1,5-dione (**5a**). Cyclomanganation of **5a** and its 1,5-di-(2-thienyl) and 1,5-di-(3-thienyl) analogues **5b** and **5c** turned out to provide novel chemistry which forms the basis of the current report, with manganation of pyridyl chalcones (cf **4**) restricted here to two which could be obtained by the condensation reaction without the formation of analogues of **5a** using the somewhat sterically crowded aryl ketones 2′,6′-dimethoxyacetophenone and 3-acetyl-2,5-dimethylthiophene.



1



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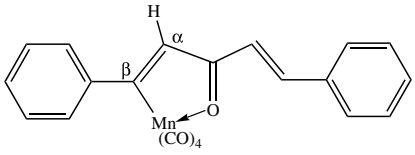

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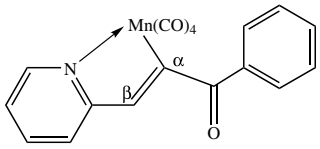

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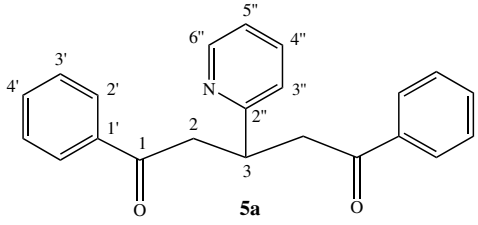
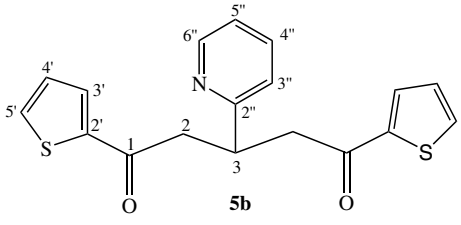
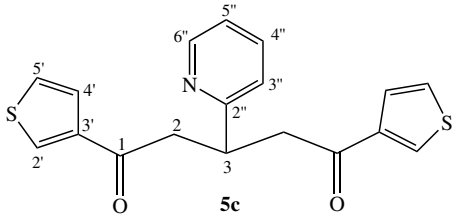


5a



5b



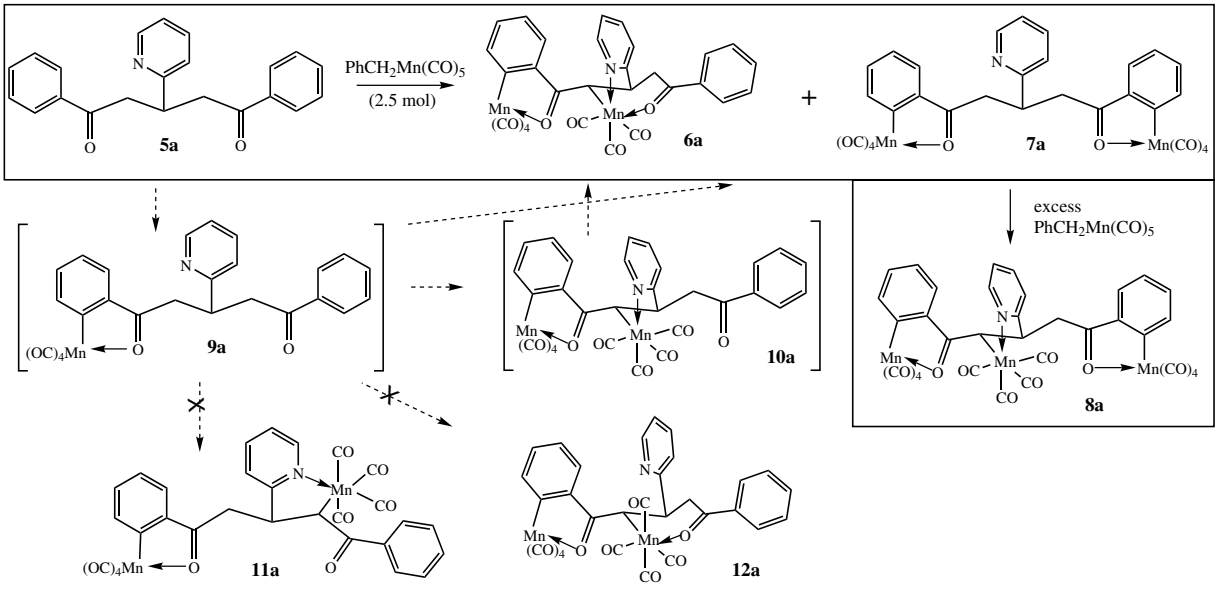
5c

2. Results and discussion

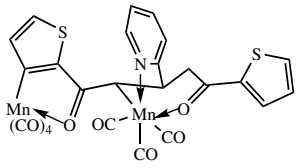
2.1. Manganation of 1,5-diaryl-3-(2-pyridyl)pentane-1,5-diones

After 1,5-diaryl-3-(2-pyridyl)pentane-1,5-dione (**5a**) was reacted overnight with 2.5 moles of $PhCH_2Mn(CO)_5$ in refluxing petroleum spirit (b.p. 60–80 °C), a yellow crystalline product was formed on cooling. Its infrared spectrum indicated the presence of the $Mn(CO)_4$ group (ν_{CO} 2073, 1983, 1922 cm^{-1}) but broadness in the latter two peaks and in particular a strong absorption at 2017 cm^{-1} suggested the presence also of $Mn(CO)_3$. The compound was characterized by NMR spectroscopy and X-ray single crystal structure analysis as [1,5-diphenyl-κC^2-3-(2-pyridyl-κN)pentan-2-yl-κC^2-1,5-dione-κO^1κO^5]tetracarbonylmanganesetricarbonylmanganese (**6a**; Scheme 1), revealing unprecedented direct cyclomanganation at a methylene (sp^3) carbon α to a ketone carbonyl group. Cooling the remainder of the reaction solution at 4 °C led to a second crop of yellow crystals whose infrared spectrum indicated only $Mn(CO)_4$ and this was identified by its simple NMR spectrum as the symmetric dimanganated compound **7a** (15%, cf 59% of **6a**).

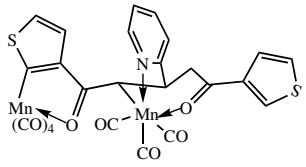
Repetition of the reaction with a larger (3 molar) excess of $PhCH_2Mn(CO)_5$ to attempt to enforce further cyclomanganation again gave crystals of **6a** in the same yield but low temperature crystallization from the residual solution now led to the tri-$Mn(CO)_4$ product **8a** (19%) without any **7a**. The implication from the consistency in the yield of **6a** between the two reactions is (Scheme 1) that once **6a** is formed it does not further manganate presumably because all of the donor groups are tied up in metal coordination. By contrast, the dimanganated **7a** is apparently still reactive enough through the uncoordinated N to further manganate with excess $PhCH_2Mn(CO)_5$ and form **8a**. The most likely sequence is as in Scheme 1, which also indicates the possibility (potential product **12a**) of ketone carbonyl initiation of the second manganation at the methylene carbon by formation of a 6-membered manganocycle, which could be followed by N-coordination to form **6a** (not shown by arrow in Scheme 1). However, the lack of detection of any of this dimanganated product (**12a**) and the absence of any literature precedence for 6-membered (as opposed to the apparently exclusive 5-membered) manganocycle formation in reactions of $PhCH_2Mn(CO)_5$ and $MeMn(CO)_5$ suggest that the ketone coordination (in **6a**) more likely occurs only after the *N*-coordinated manganation (**9a** → **10a** → **6a**): coordination of C=O to Mn in the six-membered ring probably reflects product stabilization, not manganation transition state stabilization. Not totally excludable as a route to **6a**, however, is a third alternative that, in spite of unfavourable entropy and a crowded transition state, both N and C=O become coordinated to $PhCH_2Mn(CO)_5$ prior to manganation (**9a** → **6a** without discrete formation of **10a** or **12a**; not shown in Scheme 1), although the reaction **7a** → **8a** with excess $PhCH_2Mn(CO)_5$ shows that *N*-coordinated manganation at the sp^3 methylene carbon does not *require* assistance by prior coordination of an extra ketone C=O to the metalating atom.



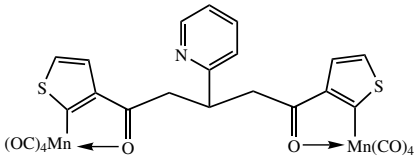
Scheme 1. Routes to di- and tri-manganated products from **5a**. Outside the reaction boxes are possible intermediates and/or products not observed but discussed in the text: in square brackets are **9a**, which via **10a** (rather than **12a**) provides the most likely route to **6a** (and to **8a** via **7a** rather than **12a**). Also shown is **11a** (not observed in competition with **6a**; reasons discussed in the text).



6b



6c



7c

Structurally, most interest in **6a** lies with the tridentate ligand coordination involving both a 5-membered *N*-coordinated manganocycle and a 6-membered (C=O)-coordinated manganocycle, and a common sp^3 carbon. This is a rare example of cyclomanganation at a saturated carbon. The only other compound we are aware of for which direct manganation by $PhCH_2$-$Mn(CO)_5$ leads to manganation at saturated carbon is another *N*-donor, 8-methylquinoline, which forms **13** [3].

Other cyclomanganated compounds with Mn bonded to saturated carbon are known [4–7], including some α to (ester) carbonyl groups [4], but none are formed by direct manganation, e.g., **14** is formed from *ortho*-manganated 2-phenyl-2-oxazoline [2-phenyl-κC^2-2-oxazoline-κ^N]tetracarbonylmanganese on thermolysis with 9-diazofluorene [7c].

Of course the sp^3 methylene carbon which becomes manganated has some degree of alkenyl (sp^2) character because of an enolic contribution associated with the adjacent carbonyl group, which would be augmented by C=O coordination to the first $Mn(CO)_4$ (**9a**; Scheme 1). This may activate the sp^3 carbon as there is no sign of the alternative dimanganated product **11a** which would be formed from reaction at the methylene carbon α to the non-coordinated C=O. The argument for metal-coordinated C=O activation of the adjacent sp^3 carbon would not be required, however, if, as discussed above, the second manganation requires *prior* coordination of both N and the second C=O to $PhCH_2Mn(CO)_5$, as geometry would then dictate that only one methylene carbon, the one next to the Mn-coordinated C=O, would be accessible to the *N*,*O*-coordinated $BzMn(CO)_3$ group. Here again, though, the lack of precedence for a 6-membered manganocyclic transition states for ketones suggests the dual-coordination mechanism would not provide special transition state stabilization. By contrast, product stabilization by coordination of the second C=O into the 6-membered manganocycle in **6a** *subsequent* to *N*-coordinated manganation is consistent with the known stability of 6-membered manganocycle products in general, e.g., as formed by ring expansion reactions of 5-membered manganocycles by insertion of SO_2 into *ortho*-manganated acetophenones to form analogues of **15** [8], or as in the case of **14** above.

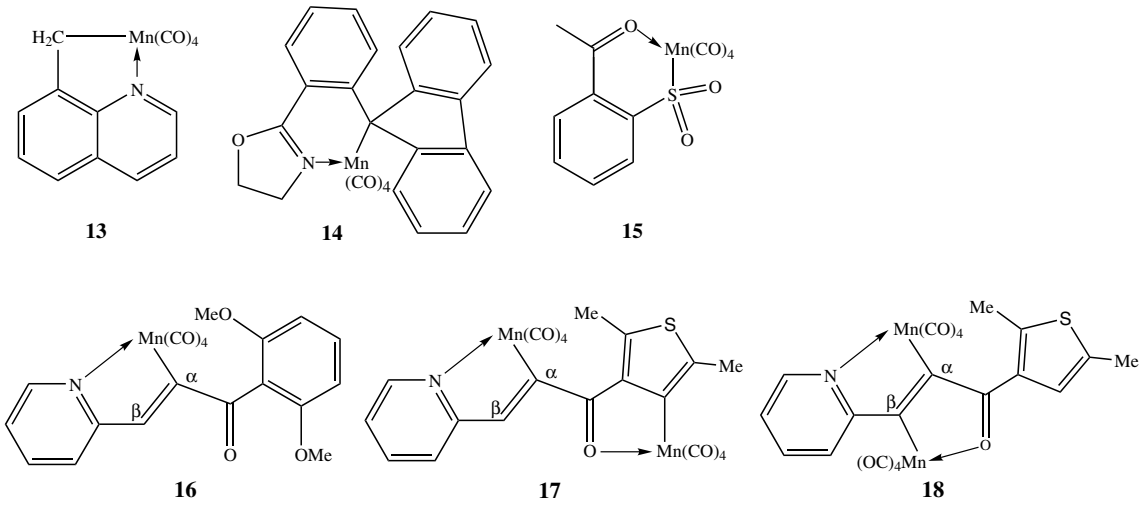
With the 2-thienyl analogue of **5a**, 3-(2-pyridyl)-1,5-di-(2-thienyl)pentane-1,5-dione (**5b**), 2.5 moles of $PhCH_2Mn(CO)_5$ gave the same type of major dimanganation product (**6b**; 84%), with no sign of the doubly *ortho*-aryl-manganated analogue of **7a**.

By contrast, under the same conditions, the 3-thienyl analogue 3-(2-pyridyl)-1,5-di-(3-thienyl)pentane-1,5-dione (**5c**) gave the now expected dimanganated analogue **6c**, but only in 27% yield, with the doubly *ortho*-aryl-manganated product (**7c**) dominating slightly (35%), showing that the thienyl 2-position here competes much better with *N*-initiated manganation at the methylene carbon than does the thienyl 3-position available in the case of **5b**.

2.2. Manganation of 3-(2-pyridyl)chalcones

(*E*)-1-(2,6-Dimethoxyphenyl)-3-(2-pyridyl)prop-2-en-1-one reacted with 1 mole of benzylpentacarbonylmanganese to form the α-manganated-*N*-coordinated product [1-(2,6-dimethoxyphenyl)-3-(2-pyridyl-κ*N*)prop-2-en-2-yl-κC^2-1-one]tetracarbonylmanganese (**16**) in 84% yield in preference to the *O*-coordinated β-manganated product of the type **1**, which are normally the major products for simple chalcones [1a]. The structure of **16** is immediately evident from the (doublet) ^{13}C NMR signal for the β-carbon which is found at 199 ppm instead of around 250 ppm expected for a (singlet) β-manganated carbon by analogy with **1** and **3** [1a,1c].

For **16**, aryl orthomanganation, normally the minor outcome for simple chalcones [1a], was unavailable because of the absence of a free *ortho* site in the 2,6-dimethoxyphenyl ring. However, when a free ortho site



was provided with (*E*)-1-(2,5-dimethyl-3-thienyl)-3-(2-pyridyl)prop-2-en-1-one, dimanganation occurred readily to form **17**. There was no sign of α,β-dimanganation (**18**) here: strain effects associated with forming two fused 5-membered rings and steric repulsion with the close proximity of the Mn centers may contribute.

*2.3. Structure of [1,5-diphenyl-κC²-3-(2-pyridyl-κN)-pentan-2-yl-κC²-1,5-dione-κO¹κO⁵]tetracarbonyl-manganesetricarbonylmanganese (**6a**)*

The structure is shown in Fig. 1 and selected bond parameters are given in Table 1.

The structure shows the dione ligand has been doubly cyclomanganated, but with two very different metallocyclic rings. Mn(2) is part of an $Mn(CO)_4$ group which is attached to one of the peripheral phenyl groups and to one of the ketone oxygen atoms to give a five-membered cyclomanganated ring similar to those formed by many other aryl ketones [9]. As in the earlier examples, the ring is essentially planar with standard Mn–C and Mn–O bonds (2.044(3) and 2.034(2) Å, respectively, compared with 2.042(2) and 2.055(2) Å in orthomanganated acetophenone [10]).

The other manganese atom, Mn(1), is of more interest. It is part of a *fac*-$Mn(CO)_3$ unit that forms a five-membered cyclometallated ring through coordination to the pyridyl nitrogen atom and to C(2), which is an sp^3 carbon atom adjacent to the C=O group attached to Mn(2). This ring also incorporates another sp^3 carbon C(3) and these two atoms ensure the ring is distinctly non-planar. The coordination sphere of Mn(1) is completed by attachment of the remaining C=O group which generates an extra six-membered manganacyclic ring. The atoms Mn(1)O(5)C(5)C(4)C(3) are essentially coplanar, with C(2) displaced to give an envelope conformation overall. The Mn(1)–N(1) and Mn(1)–O(5) distances of 2.057(4) and 2.048 Å, respectively, are as expected, but the Mn(1)–C(2) distance 2.201(3) Å is ca 0.16 Å longer than for Mn–C(sp^2) distances in other manganacycles. This cannot be fully explained by the difference in the covalent radii of sp^2 and sp^3 carbon atoms (ca 0.05 Å), and suggests there is some π component in Mn–C(sp^2) bonds that is absent in the Mn–C(sp^3) ones.

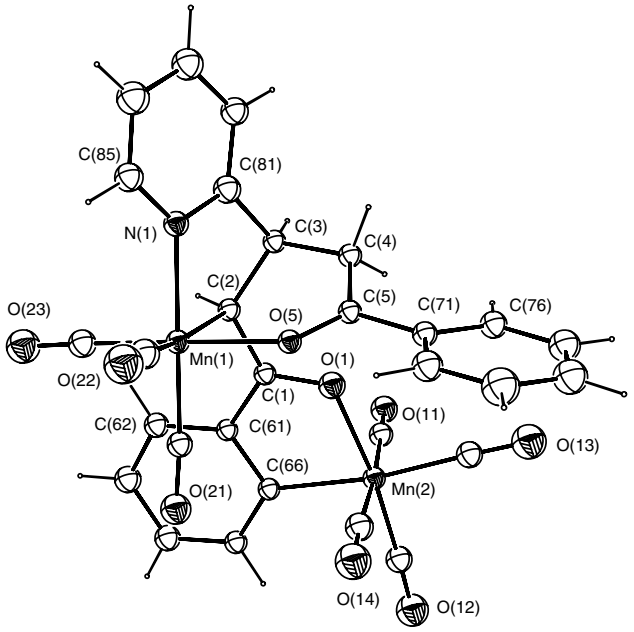


Fig. 1. Molecular structure of **6a**.

Table 1
Selected bond parameters for **6a**

Bond lengths (Å)	
Mn(1)–C(2)	2.201(3)
Mn(1)–O(5)	2.048(2)
Mn(2)–O(1)	2.034(2)
C(1)–O(1)	1.262(4)
C(1)–C(2)	1.430(6)
Mn(1)–N(1)	2.057(3)
Mn(2)–C(66)	2.044(3)
C(5)–O(5)	1.243(5)
C(2)–C(3)	1.530(5)
C(1)–C(61)	1.479(5)
Bond angles (°)	
N(1)–Mn(1)–O(5)	89.6(2)
O(5)–Mn(1)–C(2)	84.3(2)
Mn(1)–C(2)–C(1)	105.7(3)
C(1)–C(2)–C(3)	119.1(3)
C(3)–C(4)–C(5)	115.1(3)
C(66)–Mn(2)–O(1)	79.2(2)
N(1)–Mn(1)–C(2)	77.7(2)
Mn(1)–O(5)–C(5)	134.4(3)
Mn(1)–C(2)–C(3)	102.5(3)
C(2)–C(3)–C(4)	117.1(3)
Mn(2)–O(1)–C(1)	117.7(3)

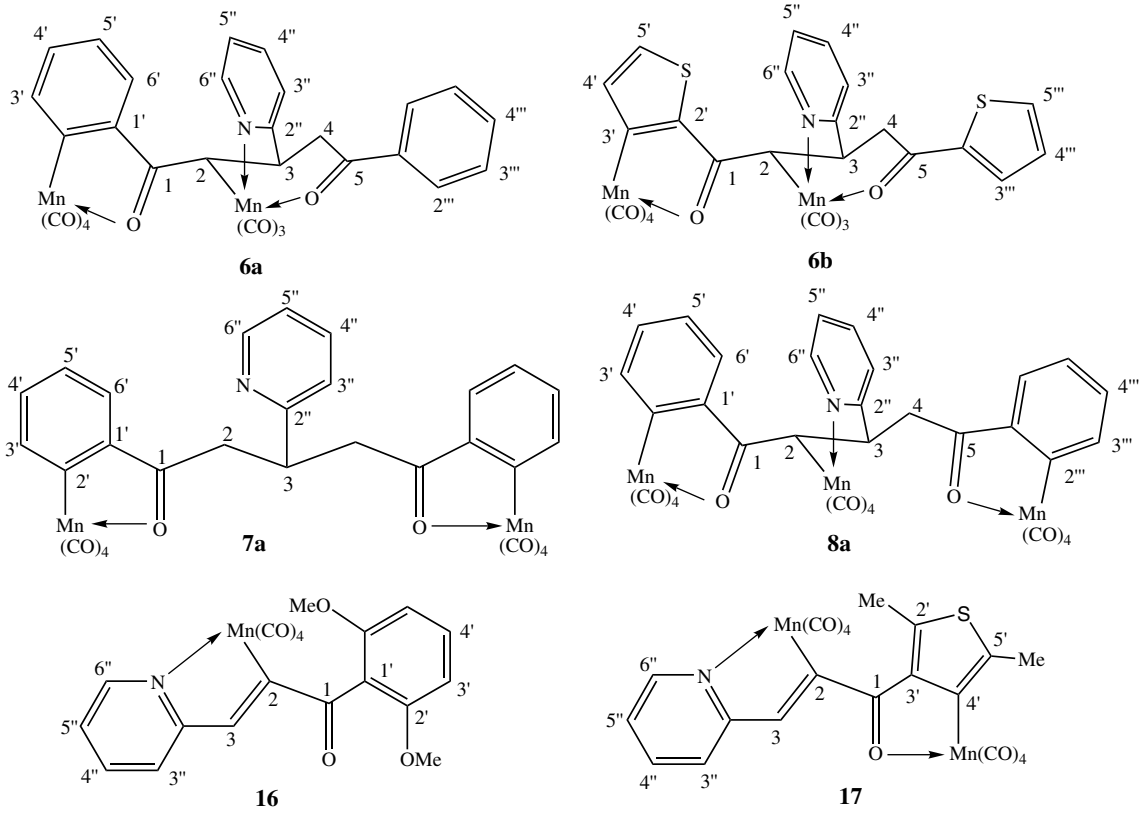
The idealized octahedral geometry of Mn(1) is distorted by N(1)–Mn(1)–C(2) and O(5)–Mn(1)–C(2) angles of 77.7(2)° and 84.3(2)°, determined by the constraints of the five- and six-membered rings, respectively. These match the equivalent angles in other cyclometallated manganese compounds, and suggest there is little extra strain in combining two different metallocyclic rings at one manganese atom in **6a**.

3. Experimental

3.1. General

Benzylpentacarbonylmanganese was prepared by the standard literature method [11]. Petroleum spirit (b.p. 60–80 °C) was redistilled, and dichloromethane and pentane used in crystallization by diffusion were of analytical grade. Other commercial reagents were used without purification. Infrared spectra (in dichloromethane) were obtained on a Digilab FTS-45 FTIR instrument. NMR spectra were recorded on a Bruker AC300 instrument.

For NMR assignments in Section 3.2.1, numbers with a double prime refer to the 2-pyridyl ring and those with a single prime to the other aryl ring(s). Because of complexity of structures in Sections 3.2.2 and 3.2.3, representative examples indicating the numbering used in NMR assignments are shown in Scheme 2.



Scheme 2. Representative structures with indicative numbering for NMR assignments.

3.2. Synthetic

3.2.1. Standard procedure for the preparation of 1,5-diaryl-3-(2-pyridyl)pentane-1,5-diones (**5**) and (*E*)-3-(2-pyridyl)prop-2-enones

Ethanol (5 mL) and a solution of sodium hydroxide (1.3 g) in water (9 mL) were mixed in a flask immersed in crushed ice. The appropriate acetophenone (ca. 30 mmol) and pyridine-2-carboxaldehyde (ca 30 mmol) were added dropwise while stirring, maintaining the temperature at about 25 °C. After stirring for a further 4 h, the mixture was left at −8 °C overnight. The crude product was filtered, washed with water until neutral to litmus, and then with small volumes of ethanol (3 × 2 mL). Recrystallization from ethanol gave the 1,5-diaryl-3-(2-pyridyl)pentane-1,5-diones (**5a**–**c**) in 50–75% non-optimised yield, or in the two cases where only a single condensation occurred, the (*E*)-3-(2-pyridyl)prop-2-en-1-ones. Elemental analyses on the manganated products provided confirmation of identity. NMR spectra indicated that the recrystallized product was pure in all cases.

1,5-Diphenyl-3-(2-pyridyl)pentane-1,5-dione (***5a***): m.p. 116 °C. ^{1}H NMR ($CDCl_3$): δ 8.43 (1H, d, J = 4.8 Hz, H6″), 7.91 (4 H, d, J = 7.7 Hz, H2′,6′), 7.51 (1H, dt, J = 7.7, 1.8 Hz, H4″), 7.46 (2H, m, H4′), 7.35 (5H, m, H3′,5′,H3″), 7.00 (1H, ddd, J = 4.2, 1.2, 1.1 Hz, H5″), 4.22 (1H, m, H3), 3.63 (2H, dd, J = 17.3, 7.7 Hz, H2a,4a), 3.42 (2H, dd, J = 17.3, 6.0 Hz, H2b,4b); ^{13}C NMR ($CDCl_3$): δ 198.6 (s, C1,5), 163.0 (s, C2″), 149.2 (d, C6″), 137.0 (s, C1′), 136.4 (d, C4″), 133.1 (d, C4′), 128.6 (d, C3′,5′), 128.1 (d, C2′,6′), 124.1 (d, C3″), 121.6 (d, C5″), 43.6 (t, C2,4), 38.2 (d, C3).

1,5-Di-(2-thienyl)-3-(2-pyridyl)pentane-1,5-dione (***5b***): m.p. 100 °C. ^{1}H NMR ($CDCl_3$): δ 8.40 (1H, d, J = 4.8 Hz, H6″), 7.66 (2H, d, J = 3.8 Hz, H3′), 7.50 (2H, d, J = 4.9 Hz, H5′), 7.45 (1H, t, J = 7.8 Hz, H4′), 7.25 (1H, d, J = 7.4 Hz, H3″), 7.00 (3H, m, H4′, H5″), 4.12 (1H, m, H3), 3.51 (2H, dd, J = 16.6, 7.8 Hz, H2a,4a), 3.32 (2H, dd, J = 16.6, 6.1 Hz, H2b,4b); ^{13}C NMR ($CDCl_3$): δ 191.4 (s, C1,5), 162.2 (s, C2″), 149.2 (d, C6″), 144.3 (s, C2′), 136.4 (d, C4″), 133.6 (d, C5′), 132.1 (d, C3′), 128.1 (d, C4′), 124.0 (d, C3″), 121.7 (d, C5″), 44.0 (t, C2,4), 38.7 (d, C3).

1,5-Di-(3-thienyl)-3-(2-pyridyl)pentane-1,5-dione (***5c***): m.p. 127 °C. ^{1}H NMR ($CDCl_3$): δ 8.45 (1H, d, J = 4.0 Hz, H6″), 8.05 (2H, dd, J = 2.8,1.2 Hz, H2′), 7.52 (1H, dt, J = 7.8, 1.8 Hz, H4″), 7.49 (2H, dd, J = 5.0, 1.2 Hz, H4′), 7.30 (1H, d, J = 7.8 Hz, H3″), 7.23 (2H, dd, J = 5.0, 2.8 Hz, H5′), 7.03 (1H, m, H5″), 4.14 (1H, m, H3), 3.49 (2H, dd, J = 16.8, 7.7 Hz, H2a,4a), 3.34 (2H, dd, J = 16.8, 7.1 Hz, H2b,4b); ^{13}C NMR ($CDCl_3$): δ 192.9 (s, C1,5), 162.6 (s, C2″), 149.2 (d, C6″), 142.3 (s, C3′), 136.4 (d, C4″), 132.2 (d, C2′), 126.9 (d, C4′), 126.2 (d, C5′), 124.0 (d, C3″), 121.7 (d, C5″), 44.7 (t, C2,4), 38.4 (d, C3).

(E)-1-(2,6-Dimethoxyphenyl)-3-(2-pyridyl)prop-2-en-1-one: m.p. 148 °C. ^{1}H NMR ($CDCl_3$): δ 8.62 (1H, d, J = 4.6 Hz, H6″), 7.69 (1H, dt, J = 7.8, 1.8 Hz, H4″), 7.52 (1H, d, J = 7.9 Hz, H3″), 7.26 (3H, m, H2,3,5″), 7.19 (1H, m, H4′), 6.54 (2H, d, J = 8.4 Hz, H3′,5′), 3.70 (6H, s, OCH_3); ^{13}C NMR ($CDCl_3$): δ 195.4 (s, C1), 157.6 (s, C2′,6′), 153.7 (s, C2″), 150.1 (d, C6″), 143.7 (d, C3), 136.7 (d, C4″), 131.9 (d, C2), 131.0 (d, C4′), 124.2 (d, C5″), 123.9 (d, C3″), 118.3 (s, C1′), 104.1 (d, C3′,5′), 55.9 (q, OCH_3).

(E)-1-(2,5-Dimethyl-3-thienyl)-3-(2-pyridyl)prop-2-en-1-one: m.p. 48 °C. ^{1}H NMR ($CDCl_3$): δ 8.65 (1H, d, J = 4.0 Hz, H6″), 7.81 (1H, d, J = 15.3 Hz, H3), 7.71 (1H, dt, J = 7.7, 1.7 Hz, H4″), 7.65 (1H, d, J = 15.3 Hz, H2), 7.44 (1H, d, J = 7.7 Hz, H3″), 7.26 (1H, t, J = 7.7 Hz, H5″), 7.17 (1H, s, H4′), 2.41 (3H, s, CH_3), 2.38 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$): δ 186.2 (s, C1), 153.4 (s, C2″), 150.1 (d, C6″), 148.2 (s, C3′), 141.5 (d, C3), 136.9 (d, C4″), 136.5 (s, C2′ or 5′), 135.3 (s, C2′ or 5′), 128.6 (d, C2), 126.3 (d, C4′), 125.2 (d, C3′), 124.2 (d, C5″), 16.0 (q, CH_3), 15.0 (q, CH_3).

3.2.2. Standard method for manganation of 1,5-diaryl-3-(2-pyridyl)pentane-1,5-diones (**5**)

Using standard Schlenk equipment, **5a**–**c** and benzylpentacarbonylmanganese (2.5–3 mol as indicated in individual cases below) were heated under reflux overnight in nitrogen-saturated petroleum spirit (b.p. 60–80 °C). On cooling, the *first product* which crystallized (**6a**–**c**) was collected by filtration and recrystallised by diffusion (dichloromethane, pentane). The filtrate solution was cooled at 4 °C overnight, and the *second product* if so obtained was collected and recrystallised by diffusion (dichloromethane, pentane).

3.2.2.1. 1,5-Diphenyl-3-(2-pyridyl)pentane-1,5-dione (***5a***) *with 2.5 mol* $PhCH_2Mn(CO)_5$. *First product*. [1,5-Diphenyl-κC^2-3-(2-pyridyl-κN)pentan-2-yl-κC^2-1,5-dione-κO^1κO^5]tetracarbonylmanganesetricarbonylmanganese (**6a**): Yellow chunky crystals (59%), decomp. 160 °C. IR: ν(CO) 2073 (m), 2017 (vs), 1983 (s, br), 1922 (s, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.76 (1H, d, J = 5.1 Hz, H6″), 7.94 (4H, m, J = 7.7 Hz, H3′, H6′, H2″,6″), 7.81 (1H, t, J = 7.0 Hz, H4″), 7.66 (1H, t, J = 7.3 Hz, H4″), 7.51 (3H, m, H3″, H3‴,5‴), 7.29 (1H, t, J = 7.1 Hz, H4′), 7.22 (1H, t, J = 7.0 Hz, H5″), 7.12 (1H, t, J = 7.1 Hz, H5′), 4.17 (1H, m, H3), 4.10 (1H, s, H2); 3.62 (2H, m, H4). ^{13}C NMR ($CDCl_3$): δ 216.9 (s, C1), 207.3 (s, C5), 184.7 (s, C2′), 172.3 (s, C2″), 152.4 (d, C6″), 145.1 (s, C1′), 141.2 (d, C3′), 138.8 (d, C4″), 135.4 (d, C4‴), 135.0 (s, C1″), 131.2 (d, C4′), 129.1 (d, C3‴,5‴), 128.5 (d, C2‴,6‴), 127.0 (d, C6′), 122.9 (d, C5′), 122.3 (d, C5″), 121.9 (d, C3″), 54.0 (d. C2), 44.2 (d, C3), 42.5 (t, C4). This compound

was further characterised by a single crystal X-ray structure determination (see below).

Second product: [1,5-Diphenyl-κC^2-3-(2-pyridyl)pentane-1,5-dione-κO^1κO^5]bis-(tetracarbonylmanganese) (**7a**): Yellow crystals (15%), decomp. 170 °C, identified by spectra only: IR: *ν*(CO) 2082 (m), 1995 (s, br), 1938 (s, br) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 8.38 (1H, d, *J* = 4.2 Hz, H6″), 8.05 (2H, d, *J* = 7.5 Hz, H3′), 7.86 (2H, d, *J* = 7.8 Hz, H6′), 7.54 (1H, dt, *J* = 7.6, 1.7 Hz, H4″), 7.39 (2H, dt, *J* = 7.4, 1.2 Hz, H4′), 7.15 (2H, dt, *J* = 7.5, 1.0 Hz, H5′), 7.06 (2H, m, H3″,5″), 4.02 (1H, m, H3),3.62 (2H, dd, *J* = 16.2, 8.9 Hz, H2a,4a), 3.30 (2H, dd, *J* = 16.2, 5.6 Hz, H2b,4b). ^{13}C NMR ($CDCl_3$): *δ* 216.9 (s, C1,5), 194.3 (s, C2′), 160.4 (s, C2″), 149.5 (d, C6″), 145.1 (s, C1′), 141.6 (d, C3′), 136.5 (d, C4″), 134.0 (d, C4′), 131.4 (s, C6′), 123.9 (d, C5′), 123.6 (d, C3″), 122.2 (d, C5″), 42.0 (t, C2,4), 40.3 (d, C3).

*3.2.2.2. 1,5-Diphenyl-3-(2-pyridyl)pentane-1,5-dione (**5a**) with 3 mol $PhCH_2Mn(CO)_5$. First product.* **6a** (58%): spectral data as above.

Second product. [1, 5-Diphenyl-κ$C^{2'}$ κ$C^{2'''}$-3-(2-pyridyl-κ*N*)pentan-2-*yl*-κC^2-1, 5-dione-κO^1κO^5]tris-(tetracarbonylmanganese) (**8a**): Mustard yellow crystals (19%), decomp. 178 °C. Anal. Found: C, 49.05; H, 1.70. $C_{34}H_{16}NO_{14}Mn_3$ calc.: C, 49.39; H, 1.95%. IR: *ν*(CO) 2083 (m), 2074 (m), 1993 (s, br), 1944 (s, br), 1929 (s, br) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 9.00 (1H, d, *J* = 5.6 Hz, H6″), 8.23 (1H, d, *J* = 7.5 Hz, H3‴), 8.14 (3H, m, *J* = 7.7 Hz, H3′, H4″, H6‴), 7.80 (1H, d, *J* = 7.9 Hz, H6′), 7.62 (3H, m, H3″, H5″, H5‴), 7.47 (1H, dt, H4′), 7.34 (1H, dt, *J* = 8.0, 1.0 Hz, H4‴), 7.23 (1H, dt, *J* = 7.3, 1.2 Hz, H5′), 4.86 (1H, m, H3), 4.76 (1H, d, *J* = 9.9 Hz, H2), 4.31 (1H, dd, *J* = 19.5, 3.8 Hz, H4a); 3.84 (1H, dd, *J* = 19.5, 4.4 Hz, H4b). ^{13}C NMR ($CDCl_3$): *δ* 222.2 (s, CO), 221.9 (s, CO), 219.1 (s, C1), 217.1 (s, C5), 215.0 (s, CO), 214.0 (s, CO), 213.6 (s, CO), 213.4 (s, CO), 212.8 (s, CO), 212.3 (s, CO), 193.0 (s, C2″), 186.9 (s, C2′), 172.5 (s, C2″), 155.0 (d, C6″), 146.7 (s, C1′ or C5′), 146.5 (S, C1′ or C5′), 141.9, (d, C3′ or C3‴), 141.7 (d, C3′ or C3‴), 139.4 (d, C4″), 135.0 (d, C4‴), 133.0 (d, C4′), 132.7 (d, C6‴), 128.1 (d, C6′), 124.8 (d, C5‴), 124.3 (d, C3″), 124.2 (d, C5′), 123.7 (d, C5″), 48.6 (d, C2), 46.9 (d, C3), 42.9 (t, C4).

*3.2.2.3. 1,5-Di-(2-thienyl)-3-(2-pyridyl)pentane-1,5-dione (**5b**) with 2.5 mol $PhCH_2Mn(CO)_5$. First product.* [1,5-Di(2-thienyl-κC^3)-3-(2-pyridyl-κ*N*)pentan-2-yl-κC^2-1,5-dione-κO^1κO^5]tetracarbonylmanganesetricarbonylmanganese (**6b**): Yellow crystals (84%), decomp. 174 °C. Anal. Found: C, 47.99; H, 2.94; N, 2.28. $C_{26}H_{13}S_2NO_{10}Mn_2$ calc.: C, 47.71; H, 2.08; N, 2.23%. IR: *ν*(CO) 2078 (m), 2015 (vs), 1990 (s, br), 1921 (vs, br) cm^{-1}. ^1H NMR (CD_3COCD_3): *δ* 9.02 (1H, d, *J* = 5.3 Hz, H6″), 8.24 (1H, d, *J* = 4.7 Hz, H3‴), 8.13 (2H, m, H4″, H5‴), 7.99 (1H, d, *J* = 5.0 Hz, H5′), 7.91 (1H, d, *J* = 7.7 Hz, H3″), 7.52 (2H, m, H4′, H5″), 7.41 (1H, t, *J* = 5.6 Hz, H4‴), 4.43 (1H, t, *J* = 3.7 Hz, H3), 4.24 (1H, s, H2); 4.13 (1H, dd, *J* = 14.1, 4.3 Hz, H4a), 4.02 (1H, dd, *J* = 14.1, 3.0 Hz, H4b). ^{13}C NMR (CD_3COCD_3): *δ* 213.3 (s, CO), 209.9 (s, C1), 201.7 (s, C5), 189.6 (s, C3′), 173.0 (s, C2″), 153.2 (d, C6″), 142.9 (s, C2″), 140.8 (s, C2′), 140.0 (d, C4″), 138.7 (d, C3‴), 137.1 (d, C4′), 135.9 (d, C5‴), 133.3 (d, C5′), 129.9 (d, C4‴), 123.5 (d, C5″), 123.4 (d, C3″), 55.3 (d, C2), 44.8 (d. C3), 43.2 (t, C4).

No second product was obtained on cooling the filtrate solution in this case.

*3.2.2.4. 1,5-Di-(3-thienyl)-3-(2-pyridyl)pentane-1,5-dione (**5c**) with 2.5 mol $PhCH_2Mn(CO)_5$. First product.* [1,5-Di(3-thienyl-κC^2)-3-(2-pyridyl-κ*N*)pentan-2-yl-κC^2-1,5-dione-κO^1κO^5]tetracarbonylmanganesetricarbonylmanganese (**6c**): Yellow crystals (27%), decomp. 198 °C. IR: *ν*(CO) 2084 (m), 2015 (vs), 1999 (s, br), 1919 (vs, br) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 8.78 (1H, d, *J* = 5.4 Hz, H6″), 8.12 (1H, d, *J* = 1.6 Hz, H2‴), 7.79 (1H, t, *J* = 7.6 Hz, H4″), 7.62 (1H, d, *J* = 5.0 Hz, H4′), 7.50 (2H, m, H3″, H4‴), 7.43 (1H, d, *J* = 5.0 Hz, H5′), 7.36 (1H, m, H5‴), 7.22 (1H, t, *J* = 7.0 Hz, H5″), 4.15 (1H, dd, *J* = 4.7, 3.0 Hz, H3), 3.87 (1H, s, H2); 3.51 (2H, ddd, *J* = 16.7, 4.7, 3.0 Hz, H4a, H4b), 4.02 (1H, dd, *J* = 14.1, 3.0 Hz, H4b). ^{13}C NMR ($CDCl_3$): *δ* 214.4 (s, C2′), 208.9 (s, C1), 200.7 (s, C5), 172.3 (s, C2″), 152.5 (d, C6″), 140.3 (s, C3′ or C3‴), 134.4 (d, C2‴), 131.4 (d, C5′), 127.4 (d, C5‴), 126.6 (d, C4‴), 124.5 (d, C4′), 122.3 (d, C5″), 121.8 (d, C3″), 54.8 (d, C2), 44.2 (d. C3), 43.5 (t, C4).

Second product. [1,5-Di(3-thienyl-κC^2)-3-(2-pyridyl)-pentane-1,5-dione-κO^1κO^5]bis-(tetracarbonylmanganese) (**7c**): Yellow crystals (35%), m.p. 130 °C. Anal. Found: C, 47.38; H, 2.26; N, 2.18. $C_{26}H_{13}S_2NO_{10}Mn_2$ calc.:C, 47.50; H, 1.99; N, 2.13%. IR: *ν*(CO) 2092 (m), 2009 (vs, br), 1950 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 8.42 (1H, d, *J* = 4.3 Hz, H6″), 7.49 (1H, dd, *J* = 7.7, 7.5 Hz, H4″), 7.45 (2H, d, *J* = 5.0 Hz, H4′), 7.36 (2H, d, *J* = 5.0 Hz, H5′), 7.04 (1H, dd, *J* = 7.7, 4.3 Hz, H5″), 7.01 (1H, d, *J* = 7.5 Hz, H3″), 3.99 (1H, m, H3), 3.46 (2H, dd, *J* = 15.3, 8.9 Hz, H2a,4a), 3.18 (2H, dd, *J* = 15.3, 5.7 Hz, H2b,4b); ^{13}C NMR ($CDCl_3$): *δ* 219.7 (s, CO), 213.0 (s, CO), 212.7 (s, C2′), 209.2 (s, CO), 208.9 (s, CO), 206.2 (s, C1), 160.5 (s, C2″), 150.0 (d, C3′), 149.5 (d, C6″), 136.4 (d, C4″), 132.8 (d, C5′), 126.2 (d, C4′), 123.3 (d, C3″), 122.1 (d, C5″), 43.1 (t, C2), 41.1 (d, C3).

3.2.3. Manganation of β-(2-pyridyl)chalcones

Using standard Schlenk equipment, (*E*)-1-(2,6-dimethoxyphenyl)-3-(2-pyridyl)prop-2-en-1-one and benzylpentacarbonylmanganese (1.05 mol) in petroleum spirit (b.p. 60–80 °C) were heated under reflux for 2.5 h. On cooling, [1-(2,6-dimethoxyphenyl)-3-(2-pyridyl-

κ*N*)prop-2-en-2-yl-κC^2-1-one]tetracarbonylmanganese (**16**) was collected: Small orange crystals (84%), m.p. 165 °C. Anal. Found: C, 55.26; H, 3.53; N, 3.23. $C_{20}H_{14}NO_{15}Mn$ calc.: C, 55.19; H, 3.24; N, 3.22%. IR: *ν*(CO) 2079 (m), 1994 (s, br), 1941 (s) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 8.67 (1H, d, *J* = 5.3 Hz, H6″), 7.67 (1H, dt, *J* = 7.6, 1.4 Hz, H4″), 7.31 (1H, d, *J* = 5.6 Hz, H3″), 7.29 (1H, s, H3), 7.26 (1H, d, *J* = 8.4 Hz, H4′), 7.05 (1H, dt, *J* = 5.6, 1.4 Hz, H5″), 6.61 (2H, d, *J* = 8.4 Hz, H3′,5′), 3.79 (6H, s, OCH_3); ^{13}C NMR ($CDCl_3$): *δ* 203.0 (s, C1), 199.1 (s, C2), 168.0 (s, C2″), 157.1 (s, C2′,6′), 153.5 (d, C6″), 139.7 (d, C3), 137.6 (d, C4″), 130.0 (d, C4′), 123.5 (d, C3″), 121.8 (d, C5″), 121.1 (s, C1′), 104.2 (d, C3′,5′), 55.9 (q, OCH_3).

(*E*)-1-(2,5-Dimethyl-3-thienyl)-3-(2-pyridyl)prop-2-en-1-one was similarly reacted over 4 h but with 2 moles of $PhCH_2Mn(CO)_5$. After cooling the reaction mixture was filtered to remove a trace of suspended material then solvent was removed under vacuum to give an orange oil (53%) which on crystallization from petroleum spirit gave [1-(2,5-dimethyl-3-thienyl-κC^4)-3-(2-pyridyl-κ*N*)prop-2-en-2-yl-κC^2-1-one-κ*O*]bis-(tetracarbonylmanganese) (**17**): Orange crystals (53%), decomp. 163 °C. Anal. Found: C, 46.00; H, 2.00. $C_{22}H_{11}SNO_9\ Mn_2$ calc.: C, 45.93; H, 1.93%. IR: *ν*(CO) 2085 (m), 2076 (m), 2006 (vs), 1993 (sh), 1947 (s), 1928 (s) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 8.65 (1H, d, *J* = 5.3 Hz, H6″), 7.78 (1H, dt, *J* = 7.7, 1.5 Hz, H4″), 7.39 (1H, d, *J* = 7.7 Hz, H3″), 7.14 (1H, dt, *J* = 5.3, 1.5 Hz, H5″), 7.10 (1H, s, H3), 2.64 (3H, s, CH_3), 2.52 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$): *δ* 211.2 (s, C1), 195.1 (s, C), 167.2 (s, C4′), 167.0 (s, C2″), 153.6 (d, C6″), 151.5 (s, C5′), 144.6 (s, C3′), 138.4 (d, C4″), 134.8 (d, C3), 134.4 (s, C2′), 123.1 (d, C3″), 122.1 (d, C5″), 16.8 (q, CH_3), 15.9 (q, CH_3).

3.3. X-ray crystal structure determination of **6a**

Yellow crystals were obtained from CH_2Cl_2/pentane. Crystal parameters and intensity data were obtained on an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα radiation.

Crystal data. $C_{29}H_{17}Mn_2NO_9$, *M* = 633.32, monoclinic, space group $P2_1/c$, *a* = 11.321(4) Å, *b* = 13.480(2) Å, *c* = 19.365(2) Å, *β* = 109.69(2)°, *U* = 2782.4(11) $Å^3$, D_c = 1.512 g cm^{-3} for *Z* = 4, *F*(0 0 0) 1280, *μ*(Mo Kα) 8.94 mm^{-1}, *T* 291(2) K. A total of 5378 reflections were collected, $2° < 2\theta < 50°$, 4548 unique, and empirically corrected for absorption using a series of *ϕ*-scans ($T_{max,\ min}$ 0.99, 0.86).

The structure was solved and developed routinely. Refinement based on F_o converged with $R_1 = 0.0499$ for 4017 reflections with $I > 2\sigma(I)$, R_w 0.0531 for all data. Calculations were carried out using the SHELXS 86 and SHELXL 93 programs [12].

4. Supplementary material

Full details of the structure determination have been deposited with the Cambridge Crystallographic Data Centre as CCDC 261871. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www:http//www.ccdc.cam.ac.uk).

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References

[1] (a) W. Tully, L. Main, B.K. Nicholson, J. Organometal. Chem. 503 (1995) 75;
(b) W. Tully, L. Main, B.K. Nicholson, J. Organometal. Chem. 507 (1996) 103;
(c) W. Tully, L. Main, B.K. Nicholson, J. Organometal. Chem. 633 (2001) 162.
[2] (a) C.S. Marvel, L.E. Coleman, G.P. Scott, J. Org. Chem. 20 (1955) 1785;
(b) S.V. Tsukerman, K.-S. Chang, V.F. Lavrushin, Zh. Obshch. Khim. 34 (1964) 832;
(c) J.R. Carson, R.J. Carmosin, J.L. Vaught, J.F. Gardocki, M.J. Costanzo, R.B. Raffa, H.R. Almond, J. Med. Chem. 35 (1992) 2855;
(d) N. Wachetr-Jurcsak, C. Radu, K. Redin, Tetrahedron Lett. 39 (1998) 3903.
[3] M. Pfeffer, E.P. Urriolabeitia, J. Fischer, Inorg. Chem. 34 (1995) 643.
[4] P. DeShong, D.R. Sidler, P.J. Rybczynski, G.A. Slough, A.L. Rheingold, J. Am. Chem. Soc. 110 (1988) 2575.
[5] P.L. Motz, J.J. Alexander, J. Organometal. Chem. 379 (1989) 119.
[6] D. LaFrance, J.L. Davis, R. Dhawan, B.A. Arndtsen, Organometallics 20 (2001) 1128.
[7] (a) J.-P. Djukic, K.H. Dotz, M. Pfeffer, A. De Cian, J. Fischer, Organometallics 16 (1997) 5171;
(b) J.-P. Djukic, A. Maisse-Francois, M. Pfeffer, K.H. Dotz, A. DeCian, J. Fischer, Organometallics 19 (2000) 5484;
(c) J-P. Djukic, C. Michon, D. Heiser, N. Kyritsakas-Gruber, A. De Cian, K.H. Doetz, M. Pfeffer, Eur. J. Inorg. Chem. 10 (2004) 2107–2122.
[8] J.M. Cooney, C.V. Depree, L. Main, B.K. Nicholson, J. Organometal. Chem. 515 (1996) 109.
[9] L. Main, B.K. Nicholson, Adv. Met. Org. Chem. 3 (1994) 1.
[10] R.J. McKinney, G. Firestein, H.D. Kaesz, Inorg. Chem. 14 (1975) 2057.
[11] R.D. Closson, J. Kozikowski, T.H. Coffield, J. Org. Chem. 22 (1957) 598;
see also M.I. Bruce, M.J. Liddell, G.N. Pain, Inorg. Syntheses 26 (1989) 172.
[12] (a) G.M. Sheldrick, SHELXL-86, University of Gottingen, 1986;
(b) G.M. Sheldrick, SHELXL-93, University of Gottingen, 1993.