Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 2523–2530
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Manganese carbonyl-mediated reactions of azabutadienes with phenylacetylene, methyl acrylate and other unsaturated molecules

Wade J. Mace, Lyndsay Main *, Brian K. Nicholson *, Daniel J. van de Pas

Department of Chemistry, School of Science and Technology, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Received 25 February 2004; accepted 14 April 2004

Abstract

Reaction of $PhCH_2Mn(CO)_5$ with 1,4-di-aryl-1-aza-1,3-butadienes gave substituted pyrrolinonyl rings which were η^4-coordinated to a $Mn(CO)_3$ group. These are formed by intramolecular CO insertion into a (non-isolated) cyclomanganated intermediate, followed by cyclisation. Other unsaturated reagents ($PhC{\equiv}CH$, $CH_2{=}CHCOOMe$, PhNCO) gave products arising from insertion of these, including a structurally characterised tri-aryl-η^5-azacyclohexadienyl-$Mn(CO)_3$ complex from the reaction with the alkyne.

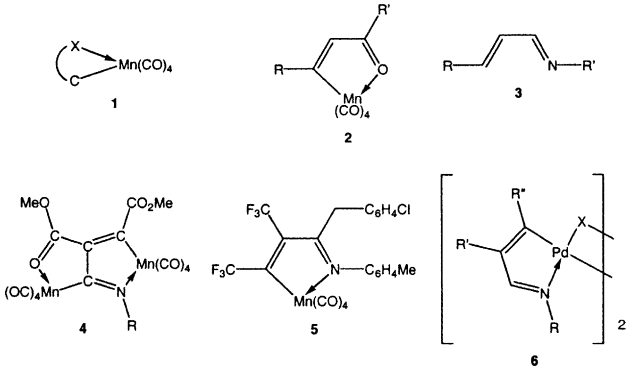
Keywords: Azabutadienes; Manganese; Carbonyl phenylacetylene

1. Introduction

Cyclomanganation of organic substrates to give complexes of the form **1** has proved to be a general process [1]. Substrates that have been examined include aryl- and hetero-aryl ketones [2] and imines [3], benzylamines [4], triphenylphosphine chalcogenides [5] and triphenylphosphine imines [6]. These complexes undergo a series of interesting reactions involving the Mn–C bond with alkenes [7], alkynes [8], organic isocyanates [9], sulfur dioxide [10] and carbon disulfide [11]. More recently, cyclomanganation studies have been extended beyond aryl substrates to reactions involving α,β-unsaturated ketones (chalcones) where compounds of the type **2** could be formed [12]. These also reacted with alkynes, in particular, to give novel products, including η^5-pyranyl- and η^5-oxocycloheptadienyl-$Mn(CO)_3$ derivatives [13].

1-Azabutadienes, **3**, are pseudo-iso-electronic with chalcones so appeared to be a potential source of new organomanganese chemistry. While there has been extensive use of azabutadienes as η^4-butadiene analogues, most of the previously reported cyclometallated azabutadiene compounds have been prepared indirectly. These include di- and tetra-ruthenium compounds [14], the dimanganese compound **4** (from $Mn_2(CO)_9(CNR)$ and DMAD [15]), and the manganese complex **5** (from $ClC_6H_4CH_2C(O)Mn(CO)_4(CNC_6H_4CH_3)$ and $CF_3CC\text{-}CF_3$) [16]. Only some orthopalladiated examples **6** have involved direct cyclometallation of an azabutadiene [17].

We now report attempts to prepare directly orthomanganated azabutadiene complexes, and their reactivity towards some unsaturated molecules.



* Corresponding author. Fax: +64-7-838-4219.
E-mail address: b.nicholson@waikato.ac.nz (B.K. Nicholson).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.04.042

2. Experimental

2.1. General

Electrospray mass spectra were recorded on a VG Platform II spectrometer, operated as detailed elsewhere [18]. Spectra were run at a cone voltage of 20 V unless otherwise specified, and in some cases Na[OMe] was added to provide ionisation [19]. NMR spectra were obtained in $CDCl_3$ on a Bruker AC400 instrument operating under standard conditions, with assignments based on COSY, HSQC and HMBC experiments. IR spectra were recorded on a Digilab FTS-40 instrument. All reactions were carried out under nitrogen, but no precautions to exclude air were taken during work-up. The azabutadiene 4-phenyl-1-*p*-tolyl-1-azabuta-1,3-diene **3a**, its 1,4-diphenyl analogue and $PhCH_2Mn(CO)_5$ were prepared by literature routes [20,21]. PLC and TLC refer to preparative and thin layer chromatography on silica gel (Merck Kieselgel 60 PF_{254}).

2.2. Reactions

2.2.1. Reaction of 4-phenyl-1-p-tolyl-1-azabuta-1,3-diene with $PhCH_2Mn(CO)_5$

A solution of the azabutadiene **3a** (51 mg, 0.23 mmol) and $PhCH_2Mn(CO)_5$ (80 mg, 0.28 mmol) in petroleum spirits (60–80 °C fraction 15 ml) was transferred to a Schlenk flask. The solution was heated under reflux for 6.5 h. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane and chromatographed (PLC), eluting with petroleum spirits/ether (1:1), to afford three fractions. The first fractions contained unreacted starting materials, while the third fraction was collected to afford the η^4-1-tolyl-3-phenylpyrrolin-2-onyl complex **7** which was recrystallised as yellow needles from diethyl ether (32 mg, 35%), m.p. 143 °C. Found: C, 62.03; H, 3.64; N, 3.62%. $C_{20}H_{14}MnNO_4$ requires C 63.36, H 3.66, N 3.82%, M 387. ν(C≡O) (heptane) 2034(s), 1962(m), 1945(m) cm^{-1}. ES-MS: (MeOH/NaOMe, −ve ion) *m/z* 386 (4%, $[M-H]^-$), 418 (100%, $[M+OMe]^-$). ^1H NMR: δ 2.41 (3H, s, CH_3), 5.98 (1H, d, $^3J_{HH}=2.4$ Hz, H4), 6.23 (1H, d, $^3J_{HH}=2.4$ Hz, H5), 7.3 (4H, m, H2″/H3″/H5″/H6″), 7.3 (1H, t, $^3J_{HH}=7.4$ Hz, H4′), 7.4 (2H, dd, $^3J_{HH}=7.5$, 7.5 Hz, H3′/H5′), 7.9 (2H, d, $^3J_{HH}=7.5$ Hz, H2′/H6′); ^{13}C NMR: δ 21.4 (CH_3), 71.2 (C3), 78.9 (C5), 83.1 (C4), 126.2 (C2′/C6′), 126.5 (C2″/C6″), 127.8 (C4′), 129.1 (C3′/C5′), 130.5 (C3″/C5″), 132.2 (C1′), 132.5 (C1″), 140.1 (C4″), 152.4(C2),221.5($Mn(CO)_3$).

2.2.2. Reaction of 4-phenyl-1-p-tolyl-1-azabuta-1,3-diene and PhC≡CH with $PhCH_2Mn(CO)_5$

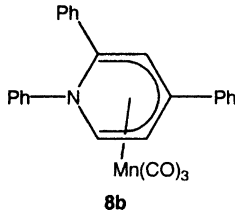
A solution of the azabutadiene **3a** (52 mg, 0.23 mmol), PhC≡CH (75 μl, 0.68 mmol) and $PhCH_2Mn$- $(CO)_5$ (87 mg, 0.30 mmol) in petroleum spirits (15 ml) was heated to reflux for three hours. The solvent was removed under vacuum, and the residue chromatographed (PLC, 1:1 petroleum spirits/ether) to give three fractions. The first main fraction afforded the azacyclohexadienyl complex **8a** which was recrystallised by vapour diffusion (ether/petroleum spirits) as a cream powder (94 mg, 87%), m.p. 176 °C. ν(C≡O) (petroleum spirits) 2025(s), 1965(m), 1946(m) cm^{-1}. ES-MS (MeOH/NaOMe, −ve ion) *m/z* 460 (27%, $[M-H]^-$), 492 (100%, $[M+OMe]^-$).

^1H NMR δ 2.22 (3H, s, CH_3), 5.01 (1H, d, $^3J_{HH}=4.2$ Hz, H6), 5.52 (1H, d, $^3J_{HH}=4.2$ Hz, H5), 6.29 (1H, s, H3), 6.58 (2H, d, $^3J_{HH}=8.1$ Hz, H2′/H6′), 6.92 (2H, d, $^3J_{HH}=8.1$ Hz, H3′/H5′), 7.30 (1H, t, $^3J_{HH}=7.3$ Hz, H4″), 7.34–7.45 (5H, m, Ar–H), 7.58 (2H, d, $^3J_{HH}=8.4$ Hz, H2″/H6″), 7.70 (2H, d, $^3J_{HH}=6.8$ Hz, H2*/H6*); ^{13}C NMR δ 20.8 (CH_3), 66.0 (C6), 82.0 (C2), 88.6 (C3), 91.7 (C5), 102.3 (C4), 115.4 (C2′/C6′), 123.9 (C2″/C6″), 127.2 (C2*/C6*), 127.9 (C4″), 128.9 (Ar–H), 129.3 (C3′/C5′), 129.4 (Ar–H), 130.3 (C1′), 136.9 (C1*), 138.1 (C1″), 153.1 (C4′), 221.7 ($Mn(CO)_3$).

The second fraction was a mixture of minor products including unreacted azabutadiene. The third fraction (11 mg) was manganese-free, but was not able to be characterized, ES-MS (MeOH/NaOMe) *m/z* 452 (100%), 905 (27%) which can be assigned as $[M-H]^-$ and $[2M-H]^-$, respectively, for $M_r=453$.

2.2.3. Reaction of l,4-diphenyl-1-azabuta-1,3-diene and PhC≡CH with $PhCH_2Mn(CO)_5$

A petroleum spirits (30 ml) solution containing $PhCH_2Mn(CO)_5$ (160 mg, 0.56 mmol), diphenylazabutadiene (100 mg, 0.48 mmol) and PhC≡CH (200 μl, 1.96 mmol) was heated under reflux for four hours. The solvent was evaporated and the residue chromatographed, eluting with ether/petroleum spirits (1:9). The main band was removed and recrystallised from hot petroleum spirits to give yellow crystals of **8b**, (68 mg, 31%). Found: C, 69.96; H, 4.28; N, 3.06%. $C_{26}H_{17}MnNO_3$ requires 69.78, H 4.05, N 3.13%, M 447. IR (petroleum spirits) ν(C≡O) 2023(s), 1965(m), 1946(m) cm^{-1}. ES-MS (MeOH/NaOMe, −ve ion) *m/z* 446 (20%, $[M-H]^-$), 478 (100%, $[M+OMe]^-$).



8b

^1H NMR δ 5.01 (1H, d, $^3J_{HH}=4.2$ Hz, H6), 5.52 (1H, d, $^3J_{HH}=4.2$ Hz, H5), 6.29 (1H, s, H3), 6.63–7.86 (Ar–H); ^{13}C NMR δ 65.3 (C6), 81.4 (C2), 88.7 (C3), 91.7 (C5), 102.4 (C4), 115.2–155.3 (Ar–C), 221.5 ($Mn(CO)_3$).

2.2.4. Reaction of 4-phenyl-1-p-tolyl-1-azabuta-1,3-diene and CH_2=$CHCO_2Me$ with $PhCH_2Mn(CO)_5$

A solution of the azabutadiene **3a** (53 mg, 0.24 mmol), CH_2=$CHCO_2Me$ (115 μl, 1.2 mmol) and $PhCH_2Mn(CO)_5$ (79 mg, 0.28 mmol) in petroleum spirits (15 ml) was transferred to a Schlenk flask under nitrogen. The solution was heated to reflux for 2 h before the solvent was removed under vacuum. The residue was chromatographed (PLC, 1:1 ethyl acetate/petroleum spirits) giving three fractions. The first and last were minor fractions containing a mixture of products (no further purification was attempted on these fractions). The second fraction contained the main product **9**, recrystallised as a yellow powder by vapour diffusion (benzene/hexane) (28 mg, 39%), m.p. 148 °C. Found: C, 63.35; H, 4.73; N, 3.27% $C_{23}H_{20}MnNO_3$ requires C 62.03, H. 4.53, N 3.15%, M 445. IR (CH_2C1_2) ν(C≡O) 2017(s), 1933(m, br) cm^{-1}, ν(C=O) 1734 cm^{-1}. ES-MS (MeOH, +ve ion) *m/z* 308 (100%, $[M–Mn(CO)_3+2H]^+$), 468 (17%, $[M+Na]^+$), 913 (11%, $[2M+Na]^+$).

^{1}H NMR δ 2.23 (1H, d, $^3J_{HH}$ = 11.8 Hz, H2), 2.40 (3H, s, Me), 3.33 (1H, d, $^3J_{HH}$ = 22.3 Hz, H5), 3.72 (1H, d, $^3J_{HH}$ = 22.2 Hz, H5), 3.83 (3H, s, OMe), 6.43 (1H, d, $^3J_{HH}$ = 11.7 Hz, H3), 7.04 (2H, d, $^3J_{HH}$ = 8.1 Hz, H2″/H6″), 7.22 (2H, d, $^3J_{HH}$ = 8.1 Hz, H3″/H5″), 7.23 (1H, m, H4′), 7.39 (2H, m, H3′/H5′), 7.53 (1H, s, H6), 7.66 (2H, m, H2′/H6′); ^{13}C NMR δ 21.1 (Me), 44.7 (C5), 51.6 (OMe), 59.9 (C2), 90.5 (C4), 102.2 (C3), 120.7 (C2″/C6″), 126.5 (C2′/C6′), 126.5 (C4′), 128.7 (C3′/C5′), 129.9 (C3″/C5″), 137.6 (C4″), 145.7 (C1′), 150.6 (C1″), 174.7 (C1), 176.4 (C6).

2.2.5. Reaction of 4-phenyl-1-p-tolyl-1-azabuta-1,3-diene and PhNCO with $PhCH_2Mn(CO)_5$

A solution of the azabutadiene **3a** (53 mg, 0.24 mmol), PhNCO (80 μl, 0.74 mmol) and $PhCH_2Mn(CO)_5$ (71 mg, 0.25 mmol) in petroleum spirits (15 ml) was heated to reflux for 2 h before the solvent was removed under vacuum. The residue was chromatographed (PLC, 1:4 ethyl acetate/petroleum spirits) to give four fractions, the first two of which were minor fractions containing unreacted starting materials. The third fraction was collected to afford **10** (24 mg, 30%) as a yellow solid. IR (CH_2C1_2) ν(C=O) 1715(br) cm^{-1}. ES-MS (MeCN, +ve ion) *m/z* 341 (100%, $[M+H]^+$), 363 (45%, $[M+Na]^+$), 681 (43%, $[2M+H]^+$), 703 (20%, $[2M+Na]^+$), 1043 (8%, $[3M+Na]^+$). ^{1}H NMR δ 2.27 (3H, s, CH_3), 3.90 (1H, s, NH), 6.05 (1H, d, $^3J_{HH}$ = 2.0 Hz, H5), 6.67 (2H, d, $^3J_{HH}$ = 8.4 Hz, H2′/H6′), 7.01 (2H, d, $^3J_{HH}$ = 8.3 Hz, H3′/H5′), 7.22 (1H, t, $^3J_{HH}$ = 7.4 Hz, H4″), 7.30 (1H, d, $^3J_{HH}$ = 2.0 Hz, H4), 7.39 (2H, m, H3″/H5″), 7.43 (2H, m, H3*/H5*), 7.46 (1H, m, H4*), 7.58 (2H, d, $^3J_{HH}$ = 7.6 Hz, H2″/H6″), 7.95 (2H, d, $^3J_{HH}$ = 6.3 Hz, H2*/H6*); ^{13}C NMR δ 20.8 (CH_3), 70.9 (C5), 115.9 (C2′/C6′), 123.4 (C2″/C6″), 125.8 (C4″), 127.9 (C2*/C6*), 128.9 (C3*/C5*), 129.4 (C3″/C5″), 129.5 (C4*), 129.7 (Cl′), 130.3 (C3′/C5′), 131.0 (Cl*), 136.8 (Cl″), 137.9 (C3), 138.2 (C4), 142.5 (C4′), 168.2 (C2)

The fourth fraction afforded a product tentatively assigned as **11** (33 mg, 30% yield) as a dark yellow solid, m.p. = 192 °C. IR (heptane) ν(C=O, C=N) 1718, 1703, 1676 cm^{-1}. ES-MS (MeOH, +ve ion) *m/z* 482 (100%, $[M+Na]^+$), 941 (36%, $[2M+Na]^+$). ^{1}H NMR δ 2.35 (3H, s, CH_3), 6.07 (CH), 6.78–7.82 (Ar–H), 8.96 (NH); ^{13}C NMR δ 21.5 (CH_3), 67.6 (CH), 120.2–140.4 (Ar–H, Ar), 153.8 (C=N), 154.6 (C=O), 168.0 (C=O).

2.2.6. Attempted reaction of 4-phenyl-1-p-tolyl-1-azabuta-1,3-diene and Bu^tNC with $PhCH_2Mn(CO)_5$

A mixture of the azabutadiene **3a** (52 mg, 0.24 mmol), Bu^tNC (200 μl, 1.8 mmol) and $PhCH_2Mn(CO)_5$ (88 mg, 0.31 mmol) in petroleum spirits (15 ml) was heated to reflux for 2 h before the solvent was removed under vacuum. The residue was chromatographed (PLC, 1:1 petroleum spirits/dichloromethane) to give three fractions. The first fraction was unreacted azabutadiene, while the second was collected to afford **12**, recrystallised as yellow crystals from hexane (15 mg, 10% yield), m.p. 96 °C. IR (heptane) ν(C≡N) 2135 cm^{-1}, ν(C≡O) 1990(m), 1939(m) cm^{-1}, ν(C=O), ν(C=N) 1713, 1679 cm^{-1}. ES-MS (MeOH, +ve ion) *m/z* 480 (100%, $[M+H]^+$). ^{1}H NMR δ 1.31 (9H, s, Bu^t), 1.39 (9H, s, Bu^t), 1.46 (9H, s, Bu^t), 3.83 (1H, d, $^2J_{HH}$ = 14.1 Hz, H3), 4.27 (1H, d, $^2J_{HH}$ = 14.1 Hz, H3), 7.17 (2H, m, H3′/H5′), 7.18 (1H, m, H4′), 7.23 (2H, m, H2′/H6′); ^{13}C NMR δ 29.9 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 31.0 ($C(CH_3)_3$), 32.7 (C3), 56.4 ($C(CH_3)_3$), 56.9 ($C(CH_3)_3$), 59.6 ($C(CH_3)_3$), 125.7 (C4′), 128.3 (C3′/C5′), 128.7 (C2′/C6′), 138.9 (C1′), 186.2 (C1), 194.8 (C2), 217.0, 221.5 224.4 (Mn–CO, Mn–$CNBu^t$) ES-MS determined that the third fraction contained a mixture of $[Mn(CNBu^t)_6]^+$ and $[Mn(CNBu^t)_5(CO)]^+$ species, and was not analysed further.

2.2.7. Reaction of 4-phenyl-1-p-tolyl-1-azabuta-1,3-diene and CS_2 with $PhCH_2Mn(CO)_5$

$PhCH_2Mn(CO)_5$ (81 mg, 0.284 mmol), the azabutadiene **3a** (54 mg, 0.243 mmol) and CS_2 (5 ml) were transferred to an ampoule which was sealed under vacuum. The ampoule was heated to 85 °C in a Carius tube for 48 h. Small yellow crystals of **13** (2 mg, 3%) crystallised from the cooled reaction mixture, and were identified by ES-MS and IR [11]. TLC of the remaining reaction mixture showed a multitude of products which were not further investigated.

2.3. X-ray crystallography

X-ray intensity data were collected on a Siemens SMART CCD diffractometer using standard procedures

and software. Empirical absorption corrections were applied (SADABS [22]). Structures were solved by direct methods and developed and refined on F^2 using the SHELX programmes [23]. Hydrogen atoms were included in calculated positions.

2.3.1. Structure of the η^4-pyrrolinonyl complex 7

Yellow needle crystals of **7** were obtained from diethyl ether.

Crystal data: $C_{20}H_{14}MnNO_4$, $M = 387.26$, monoclinic, space group $C2/c$, $a = 24.314(8)$, $b = 11.199(4)$, $c = 16.664(5)$ Å, $\beta = 131.33(3)°$, U 3407.1(19) Å^3, T 168 K, $Z = 8$, $D_{calc} = 1.510$ g cm^{-3}, μ(Mo Kα) = 0.80 mm^{-1}, F(000) 1584; 21764 reflections collected with $2° < \theta < 26°$, 3470 unique (R_{int} 0.0264) used after correction for absorption ($T_{max, min}$ 0.882, 0.686). Crystal dimensions 0.51×0.18×0.16 mm^3. Refinement on F^2 gave R_1 0.0356 [$I > 2\sigma$ (I)] and wR_2 0.0782 (all data), GoF 1.125, residual peaks (±0.26 e Å^{-3}). The structure of **7** is illustrated in Fig. 1, with selected bond parameters included in the caption to the figure.

*2.3.2. Structure of the η^5-azacyclohexadienyl complex **8b***

Yellow needle crystals of **8b** were obtained from petroleum spirits.

Crystal data: $C_{26}H_{18}MnNO_3$, $M = 447.36$, monoclinic, space group $C2/c$, $a = 21.925(7)$, $b = 10.950(4)$, $c = 17.234(6)$ Å, $\beta = 94.768(6)°$, U 4123(2) Å^3, T 163 K, $Z = 8$, $D_{calc} = 1.441$ g cm^{-3}, μ(Mo Kα) = 0.67 mm^{-1}, F(000) 1840; 24528 reflections collected with $2° < \theta < 26°$, 4067 unique (R_{int} 0.1033) used after correction for absorption ($T_{max, min}$ 1.000, 0.826). Crystal dimensions 0.36×0.18×0.12 mm^3. Refinement on F^2 gave R_1 0.0416 [$I > 2\sigma$ (I)] and wR_2 0.0450 (all data), GoF 0.935, residual peaks (±0.23 e Å^{-3}). The structure of **8b** is illustrated in Fig. 2, with selected bond parameters included in the caption to the figure.

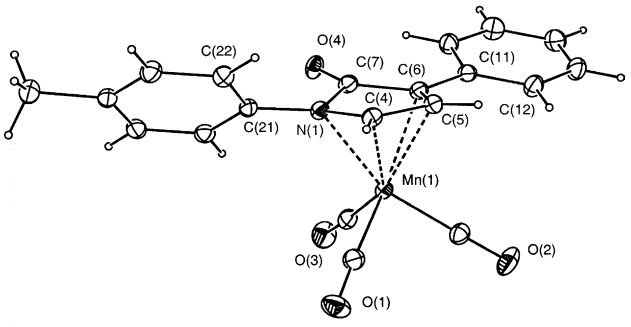


Fig. 1. The structure of the η^4-1-tolyl-3-phenylpyrrolin-2-onyl-manganese tricarbonyl complex **7**. Bond lengths include: Mn(1)–N(1) 2.102(2), Mn–C(4) 2.080(2), Mn–C(5) 2.131(2), Mn–C(6) 2.195(2), Mn···C(7) 2.375(2), C(7)–O(4) 1.214(2), C(4)–C(5) 1.394(3), C(5)–C(6) 1.421(3) Å.

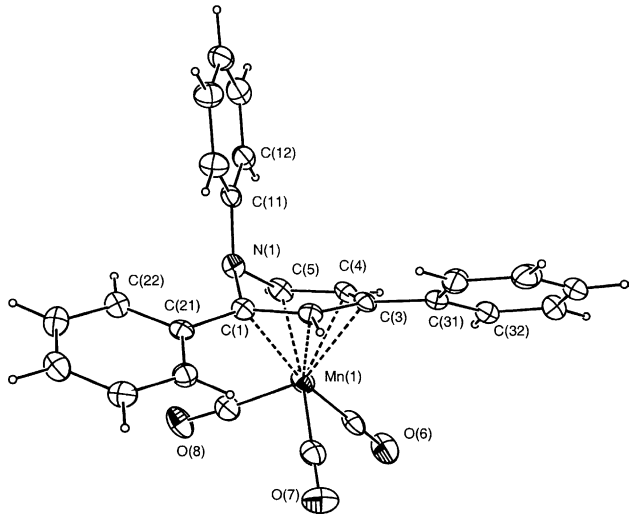


Fig. 2. The structure of the 1,2,4-triphenyl-1-azacyclohexa-2,4-dien-6-yl-manganese tricarbonyl complex **8b**. Bond lengths include: Mn(1)–C(1) 2.202(2), Mn–C(2) 2.121(2), Mn–C(3) 2.160(3), Mn–C(4) 2.107(3), Mn–C(5) 2.142(3), C(1)–N(1) 1.453(3), C(5)–N(1) 1.429(3), C(11)–N(1) 1.420(3) Å.

3. Results and discussion

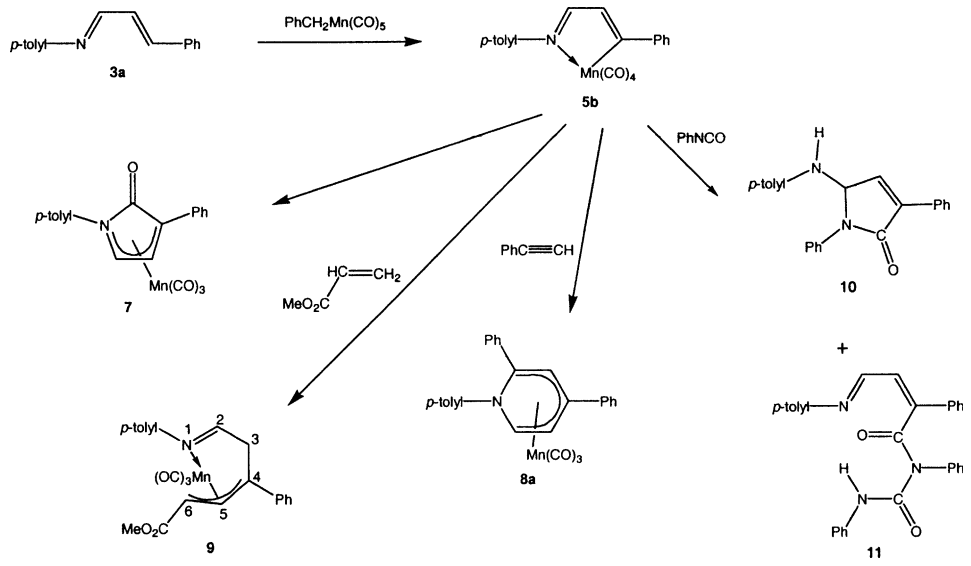
The reactions discussed in detail below are summarised in Scheme 1.

3.1. Attempted cyclomanganation of 4-phenyl-1-p-tolyl-1-azabuta-1,3-diene

When the azabutadiene **3a** was reacted with $PhCH_2Mn(CO)_5$, under the refluxing-heptane conditions used successfully for cyclometallation of chalcones, a yellow product was readily isolated. Elemental analysis and ES-MS were consistent with the expected product, a cyclometallated azabutadiene, but the infrared spectrum was not since the ν(CO) pattern was more like that of a $Mn(CO)_3$ moiety than the characteristic $Mn(CO)_4$ type.

An X-ray crystal structure determination was therefore carried out. This showed that a substituted pyrrolinonyl ring had formed and was coordinated to a $Mn(CO)_3$ group as in **7**. The structure is illustrated in Fig. 1. Clearly, the deprotonated azabutadiene group has combined with a CO ligand to form the new planar ring structure, and this acts as a five-electron donor to the manganese, with two electrons from the N atom, two from the C(4)–C(5) π bond, and one from C(6). This leaves the C═O group free of interaction with the manganese atom, although the Mn···C(7) is quite short (2.375 Å).

There appear to be no previous examples of η^4-pyrrolinonyl complexes, the closest analogues being some η^2-pyrrolinone-Fe(CO)$_4$ species [24]. This new synthesis of pyrrolinonyl rings is of interest as such five-membered rings are involved in several areas of organic chemistry



Scheme 1.

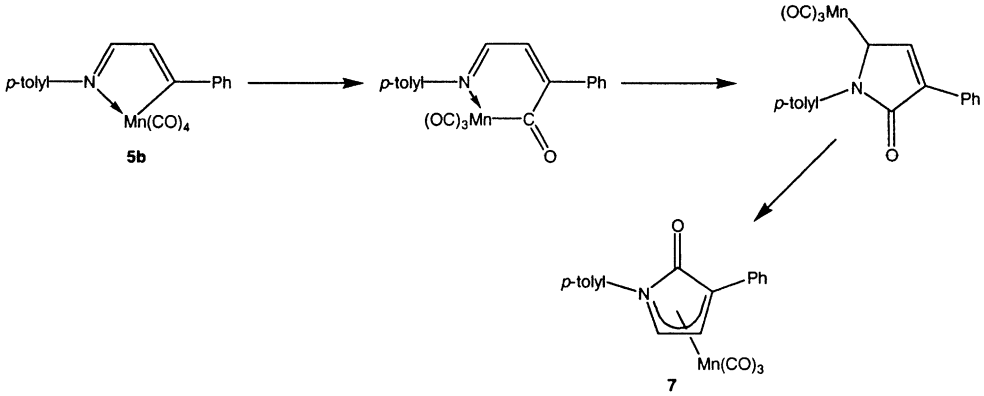
[25], and different substituents could be incorporated by choosing the appropriate azabutadiene.

A route to complex **7** can be proposed, by analogy with chalcone chemistry (Scheme 2) [13]. The first step is presumably to form the cyclometallated azabutadiene **5b**. Under the conditions, and in contrast to chalcone examples, there is rapid insertion of a CO ligand into the Mn–C σ-bond. Addition of the new Mn–C bond across the N=C bond forms the five-membered ring with the $Mn(CO)_3$ group attaching to one face in a η^4 manner to achieve an eighteen-electron configuration.

To investigate the reaction in more detail, it was repeated under milder conditions with monitoring by IR spectroscopy. When a mixture of the azabutadiene and $PhCH_2Mn(CO)_5$ was slowly heated in heptane, no change was observed until the temperature of the oil bath reached 70 °C, at which time two new IR peaks appeared at 2034 and 2076 cm^{-1}. The former of these can be attributed to the pyrrolinonyl complex **7**, while the latter is in the position expected for the highest frequency ν(CO) band for the cyclometallated azabutadiene **5b** (cf. ~2080 cm^{-1} for cyclomanganated chalcones [12]). As the reaction continued the 2034 cm^{-1} peak increased, while that at 2076 cm^{-1} was never more than a small feature. This is consistent with the process in Scheme 2, where the cyclomanganated azabutadiene is formed, but rapidly reacts further by CO insertion.

3.2. Reaction in the presence of PhC≡CH

Although the cyclomanganated complex **5b** could not be isolated, its reactivity in situ with other substrates was of interest. Several groups have shown that reactions between cyclomanganated aryl ketones or chalcones and alkynes proceed via insertion/cyclisation processes to give novel derivatives [8,13], so the corresponding reaction was investigated here. When a mixture of the azabutadiene **3a**, $PhCH_2Mn(CO)_5$ and PhC≡CH (ca. 1:1:3) was heated in petroleum spirits a reaction occurred to give a solution with ν(CO) peaks indicative of a $Mn(CO)_3$ group, but shifted ~10 cm^{-1} to lower frequencies compared with those of the



Scheme 2.

pyrrolinonyl-complex **7**. Work-up provided two products. The major one was identified spectroscopically as the η^5-azacyclohexadienyl complex **8a** formed in excellent yield. This is the N-analogue of the η^5-pyranyl complexes formed when cyclomanganated chalcones are reacted with alkynes [13], and a similar route can be assumed. This invokes the cyclomanganated azabutadiene **5b** as the first intermediate, which undergoes insertion of PhC≡CH into the Mn–C bond. Cyclisation involving the N=C bond leads to the six-membered ring with the $Mn(CO)_3$ group occupying one face (Scheme 3).

The minor product from the reaction of the azabutadiene with PhC≡CH was not identified, but appears to have arisen from CO insertion and double addition of PhC≡CH to give a species which the mass spectrum suggests has an M_r of 453.

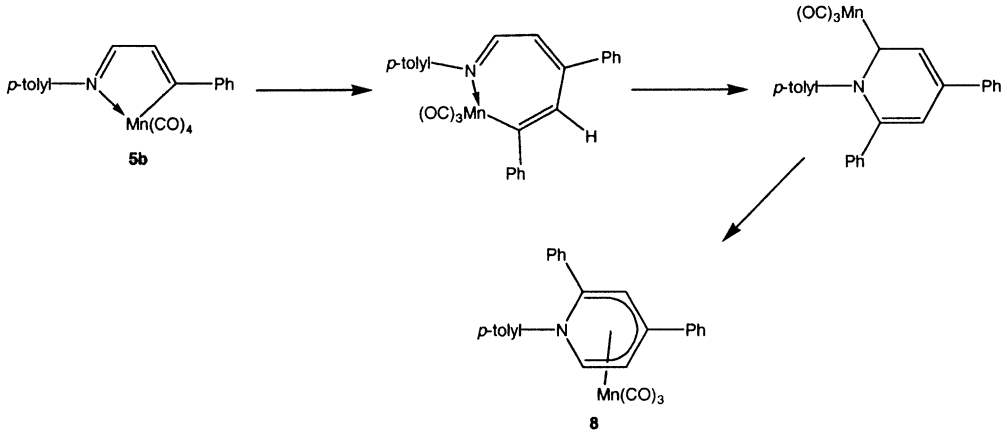
Compounds analogous to **8** have been prepared previously by reactions of alkynes with $RC_6H_4CH_2C(O)$-$Mn(CO)_4(CNC_6H_4R')$, probably via a cyclomanganated azabutadiene formed in situ by coupling the isonitrile with the first equivalent of alkyne [16]. Interestingly, the azacyclohexadienyl ligands found in that study were either η^4 or η^5, depending on the substituents. These cannot be distinguished reliably by spectroscopic means, but it seemed probable that **8a** contained an η^5 ligand in the absence of electron-withdrawing substituents on the ring. We could not prepare crystals of **8a** suitable for X-ray crystallography to confirm this, so the corresponding reaction using 1,4-diphenyl-1-azabutadiene was carried out. This gave **8b** in a completely analogous procedure and this compound crystallised well. The structure of **8b** is shown in Fig. 2 and confirms the η^5-attachment of the ligand to the manganese. The C(1)–C(5) atoms are planar to within ±0.024 Å, forming a dihedral angle with the C(1)–N(1)–C(5) plane of 50°. The Mn–C bond distances range from 2.107(2) to 2.202(3) Å, average 2.146 Å, which indicates slightly stronger bonding of the ring than in the related (η^5-pyranyl)$Mn(CO)_3$ complexes where the average Mn–C distance was 2.188 Å [13]. The structure of **8b** is directly comparable to the η^5-azacyclohexadienyl examples with other substituents reported by Homrighausen et al. [16].

3.3. Reaction in the presence of CH_2=CHCOOMe

Activated alkenes are also known to react with cyclomanganated substrates derived from aryl ketones and chalcones [7,13]. A mixture of the azabutadiene **3a**, $PhCH_2Mn(CO)_5$ and CH_2=CHCOOMe reacted to give one main product which was characterised spectroscopically as **9** in moderate yield. ES-MS and elemental analysis confirmed the formula as a combination of one CH_2=CHCOOMe, one deprotonated azabutadiene molecule and one $Mn(CO)_3$ fragment, while IR data confirmed a $Mn(CO)_3$ unit and showed from the ν(C=O) at 1734 cm^{-1} that the carboxylate group was not coordinated to the metal. A peak at 1699 cm^{-1} can be assigned to a non-conjugated C=N bond. This information, and a full 2-D NMR study, leads to the structure **9**, in which the CH_2=CHCOOMe has coupled to the azabutadiene through C-4 to give a disubstituted methyl 7-azahepta-3,6-dien-2-yloate ligand. This is coordinated to the $Mn(CO)_3$ group via an η^3-allyl interaction, with the remaining two electrons coming from the N atom. Again the formation of this species can be explained by initial formation of the cyclomanganated complex **5b**, followed by insertion of the alkene into the Mn–C bond and subsequent rearrangement giving the product. When an orthomanganated chalcone was reacted with CH_2=CHCOOMe in CCl_4 the main product was a substituted methyl 7-oxo-hepta-2,6-dienoate, which is the protio-demetallated equivalent of **9** [12].

3.4. Reaction in the presence of PhNCO

Liebeskind et al. [9] reacted orthomanganated substrates with PhNCO and showed that insertion followed by cyclisation led to phthalimidines. In the present system, PhNCO with $PhCH_2Mn(CO)_5$ and the azabutadiene gave two organic products, both in



Scheme 3.

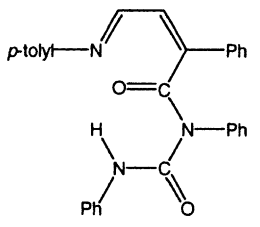
about 30% yield. The first of these showed an $[M+H]^+$ peak at *m/z* 341 in the ES-MS, giving a mass of 340 which corresponds to a combination of one PhNCO and one azabutadiene molecule. The IR spectrum showed a peak at 1715 cm^{-1} assigned to a free C=O group, and the NMR spectra were consistent with the structure **10**. This can be explained by an insertion of PhNCO into the Mn–C bond of **5b**, followed by cyclisation involving the imine carbon atom to give a five-membered ring. Subsequent protio-demetallation would give **10**.

The other product from the reaction was shown to have a mass of 459 from ES-MS. This equates to a combination of one azabutadiene molecule with two PhNCO molecules, presumably via a double insertion process. The IR spectrum contained three peaks in the C=O or C=N region. A possible structure is shown (**11**) but this could not be confirmed from NMR data so should be regarded as a tentative assignment only.

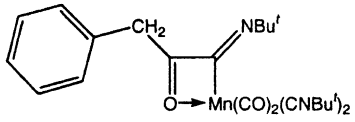
3.5. Reaction in the presence of Bu^tNC or CS_2

These substrates were also examined as "one-pot" reagents. However in neither case were products derived from the azabutadiene isolated. Bu^tNC gave a low yield of a complex **12** which is not unexpected from a reaction between $PhCH_2Mn(CO)_5$ and an isonitrile, based on other studies of $RMn(CO)_5$ compounds with isonitriles [26]. The formation of **12** involves step wise insertion of first a CO ligand and secondly a Bu^tNC one, with further replacement of two terminal carbonyl groups by isonitriles. (An isomer of **12** with the inserted CO and Bu^tNC interchanged cannot be excluded spectroscopically, but is less likely.) It appears that isonitriles are too effective as Lewis bases and react with $PhCH_2Mn(CO)_5$ before the reaction with the azabutadiene to form **5b** can take place.

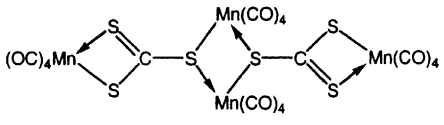
In a rather unspecific reaction, CS_2 gave a low yield of the trithiocarbonate–tetramanganese compound **13**, which has been found in similar reactions with other cyclomanganated substrates [11].



11



12



13

3.6. Summary

Although no cyclomanganated azabutadiene derivative **5b** could be isolated, it appears that this is the first-formed compound in the reaction of **3a** with $PhCH_2Mn(CO)_5$. This provides an activated form of the azabutadiene for subsequent coupling. A survey of "one pot" reactions between an azabutadiene and unsaturated substrates in the presence of $PhCH_2Mn(CO)_5$ shows that useful new compounds can be formed.

It is interesting that the three unsaturated molecules PhC≡CH, CH_2=CHCOOMe and PhNCO all appear to insert initially into the Mn–C bond of a pre-formed **5b** to give a seven-membered metallocyclic ring intermediate, but that reactions then proceed differently. The alkyne-intermediate cyclises by attack at the imine nitrogen atom to give a six-membered ring, the PhNCO-intermediate attacks at the imine carbon atom to give a five-membered ring, while the alkene-derived species does not undergo a cyclisation reaction at all. Further work with other azabutadienes and other unsaturated molecules is underway to determine the factors that affect this reactivity.

Acknowledgements

We thank Dr. Jan Wikaira and Professor Ward Robinson, University of Canterbury, for collection of X-ray intensity data.

Appendix A. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 237998 and 237999. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.04.042.

References

[1] L. Main, B.K. Nicholson, Adv. Metal-Org. Chem. 3 (1994) 1.
[2] R.J. McKinney, G. Firestein, H.D. Kaesz, Inorg. Chem. 14 (1975) 3066;
J.M. Cooney, L.H.P. Gommans, L. Main, B.K. Nicholson, J. Organomet. Chem. 349 (1988) 197;
J.M. Cooney, L.H.P. Gommans, L. Main, B.K. Nicholson, W. Tully, L. Main, B.K. Nicholson, J. Organomet. Chem. 634 (2001) 157.

[3] R.L. Bennett, M.I. Bruce, B.L. Goodall, M.Z. Iqbal, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1972) 1787;
R.L. Bennett, M.I. Bruce, I. Matsuda, Aust. J. Chem. 28 (1975) 1265;
C. Morton, D.J. Duncalf, J.P. Rourke, J. Organomet. Chem. 530 (1997) 19;
A. Bohm, K. Sunkel, K. Polborn, W. Beck, J. Organomet. Chem. 552 (1998) 237.
[4] R.G. Little, R.J. Doedens, Inorg. Chem. 12 (1973) 844;
M. Pfeffer, E.P. Urriolabeitia, J. Fischer, Inorg. Chem. 34 (1995) 643.
[5] G.J. Depree, N.D. Childerhouse, B.K. Nicholson, J. Organomet. Chem. 533 (1997) 143.
[6] M.A. Leeson, B.K. Nicholson, M.R. Olsen, J. Organomet. Chem. 579 (1999) 243.
[7] L.H.P. Gommans, L. Main, B.K. Nicholson, J. Chem. Soc., Chem. Commun. (1987) 761;
R.C. Cambie, M.R. Metzler, P.S. Rutledge, P.D. Woodgate, J. Organomet. Chem. 429 (1992) 59.
[8] L.S. Liebeskind, J.R. Gasdaska, J.S. McCallum, S.J. Tremont, J. Org. Chem. 54 (1989) 669;
N.P. Robinson, L. Main, B.K. Nicholson, J. Organomet. Chem. 364 (1989) C37;
R.C. Cambie, M.R. Metzler, P.S. Rutledge, P.D. Woodgate, J. Organomet. Chem. 429 (1992) 41.
[9] L.S. Liebeskind, S.A. Johnson, J.S. McCallum, Tetrahedron Lett. 31 (1990) 4397.
[10] J.M. Cooney, C.V. Depree, L. Main, B.K. Nicholson, J. Organomet. Chem. 515 (1996) 109.
[11] W. Mace, L. Main, B.K. Nicholson, M. Hagyard, J. Organomet. Chem. 664 (2002) 288.
[12] W. Tully, L. Main, B.K. Nicholson, J. Organomet. Chem. 503 (1995) 75.
[13] W. Tully, L. Main, B.K. Nicholson, J. Organomet. Chem. 507 (1996) 103;
W. Tully, L. Main, B.K. Nicholson, J. Organomet. Chem. 633 (2001) 162.
[14] L.H. Polm, W.P. Mul, C.J. Elsevier, K. Vrieze, M.J.N. Christopherson, C.H. Stam, Organometallics 7 (1988) 423;
W.P. Mul, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, Inorg. Chem. 30 (1991) 4152;
C.J. Elsevier, W.P. Mul, K. Vrieze, Inorg. Chim. Acta 198 (1992) 689;
W. Imhof, J. Chem. Soc., Dalton Trans. (1996) 1429.
[15] R.D. Adams, M. Huang, Organometallics 14 (1995) 506.
[16] C.L. Homrighausen, J.J. Alexander, J.A. Krause Bauer, Inorg. Chim. Acta 334 (2002) 419.
[17] S. Tenreiro, G. Alberdi, J. Martinez, M. Lopez-Torres, J.M. Ortigueira, M.T. Pereira, J.M. Vila, Inorg. Chim. Acta 342 (2003) 145.
[18] W. Henderson, B.K. Nicholson, L.J. McCaffrey, Polyhedron 17 (1998) 4291.
[19] W. Henderson, J.S. Mclndoe, B.K. Nicholson, P.J. Dyson, J. Chem. Soc., Dalton Trans. (1998) 519.
[20] H.-J. Knölker, G. Baum, N. Foitzik, H. Goesmann, P. Gonser, P.G. Jones, H. Röttele, Eur. J. Inorg. Chem. (1998) 993.
[21] M.I. Bruce, M.J. Liddell, G.N. Pain, Inorg. Synth. 26 (1989) 172.
[22] R.H. Blessing, Acta Cryst. A 51 (1995) 33.
[23] G.M. Sheldrick, SHELX-97 Programs for the Solution and Refinement of Crystal Structures, University of Gottingen, Germany, 1997.
[24] R. Siebenlist, M. de Beurs, N. Feiken, H.-W. Fruhauf, K. Vrieze, Organometallics 19 (2000) 3032;
A.D. Cuiper, M. Brzostowska, J.K. Gawronski, W.J.J. Smeets, A.L. Spek, H. Hiemstra, R.M. Kellogg, B.L. Feringa, J. Org. Chem. 64 (1999) 2567.
[25] D. Witthaut, R. Frohlich, H.J. Schafer, Angew. Chem., Int. Ed. Eng. 40 (2001) 4212.
[26] P.L. Motz, J.J. Alexander, D.M. Ho, Organometallics 8 (1989) 2589;
D.W. Kuty, J.J. Alexander, Inorg. Chem. 17 (1978) 1489;
P.L. Motz, J.P. Williams, J.J. Alexander, D.M. Ho, J.S. Ricci, W.T. Miller, Organometallics 8 (1989) 1523;
T.M. Becker, J.J. Alexander, J.A. Krause Bauer, J.L. Nauss, F.C. Wireko, Organometallics 18 (1999) 5594.