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An orthomanganation route to 2-substituted derivatives of *N*-methyl-1, 8-naphthalimide

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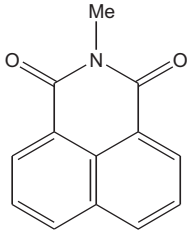
ABSTRACT

N-methyl naphthalimide can be readily cyclomanganated at the 2-position, directed by the adjacent amide O atom. Di-cyclomanganation also occurs readily to attach $Mn(CO)_4$ groups at both 2, 7 positions. An X-ray structure determination of the mono-substituted example confirmed the five-membered metallocyclic ring. Cleavage of the Mn–C bond by $HgCl_2$ or ICl generates 2-substituted HgCl or I derivatives respectively. Reaction of the mono-cyclomanganated *N*-methyl naphthalimide with phenylacetylene gives an (η^5-cyclohexadienyl)$Mn(CO)_3$ complex where the cyclohexadienyl ring has formed by two PhCCH adding in a formal [2 + 2 + 2] process across the C(1)–C(2) bond of the naphthalimide, breaking the aromaticity of the naphthalene ring as shown by a single crystal structure determination.

1. Introduction

The chemistry of *N*-alkyl-1,8-naphthalimides (for example the *N*-methyl compound **1**, also known as *N*-methyl-1,8-naphthalenedicarboximide) is well-developed. Derivatives find application as colorimetric and fluorescent sensors [1–3], and have promising chemotherapeutic properties [4,5]. Their photophysical properties are also of interest for electrochemical applications [6].



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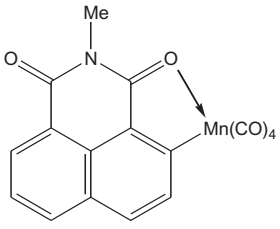
A very large number of papers (>10,000) discuss derivatives substituted at the 4-position, but in contrast there are very few 2-substituted examples (~100 papers) because of a paucity of synthetic routes. There are presently 41 structures reported for 4-substituted *N*-alkyl-1,8-naphthalimides, but none for 2-substituted analogues in the CCDC files [7].

Cyclometalation is a useful method of directing reactions at specific sites (for a recent review see Ref. [8]). We have previously reported extensively on the use of cyclomanganation of aryl ketones, amides, aldehydes, and other substrates as a means of specifically directing reactions at the ortho position of the aromatic ring [9–15], and as an extension of these studies have now examined **1** as a substrate.

We herein report the directed mono- and di-cyclomanganation of **1** at the 2-positions to give **2** and **3**, and demonstrate the use of the new complex **2** as an intermediate for preparing 2-halo- and 2-(chloromercurio)-*N*-alkyl-1,8-naphthalimides. The reaction of **2** with alkynes is also discussed, with PhCCH leading to dearomatisation of the naphthalene core.



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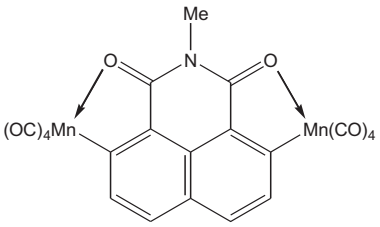

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2. Experimental details

2.1. General procedures

Spectroscopic data were obtained on a Perkin–Elmer Spectrum 100 FTIR and a Bruker BRX400 NMR, the latter with samples dissolved in $CDCl_3$. ESI-MS were from a Bruker MicrOTOF instrument, with solutions made up in methanol, operated under standard conditions. NaOMe was added to aid ionisation for the metal carbonyl samples [16]. $PhCH_2Mn(CO)_5$ was prepared by the literature method [17] and naphthalic anhydride and the alkynes were purchased from Aldrich. Chromatography was carried out on 20 × 20 cm silica gel plates. Petroleum spirit refers to a 60–80 °C fraction. Reactions were carried out under a nitrogen atmosphere in Schlenk equipment, but no precautions to exclude air were taken during work-up.

2.2. Preparation of N-methyl-1,8-naphthalimide (**1**)

1,8-Naphthalic anhydride (2.0 g, 0.01 mol) was dissolved in absolute ethanol (150 mL) and 5 mL of 25% $MeNH_2$(aq) was added. The solution was stirred at room temperature for 3 d, and the solid product which had crystallised from the reaction mixture was filtered and dried to give *N*-methyl-1,8-naphthalimide (2.2 g, 100%), pure by IR (KBr disc, $\nu_{C=O}$ 1701 m, 1668 vs cm^{-1}), ^1H NMR [δ 3.55 s ($-CH_3$), 7.74 apparent t (dd), 8.19 dd, 8.58 dd ($-C-H$)], ^{13}C NMR [δ 27.0 ($-CH_3$), 126.9, 131.2, 133.9 (all $-C-H$), 122.6, 128.1, 131.6 (quart *C*), 164.5 (*C*=O)] and ESI-MS [*m*/*z* 212.068 $[M + H]^+$ (calc 212.071), *m*/*z* 234.047 $[M + Na]^+$ (calc 234.052)].

2.3. Cyclomanganation of N-methyl-1,8-naphthalimide

A mixture of $PhCH_2Mn(CO)_5$ (0.51 g, 1.78 mmol) and *N*-methyl-*1,8*-naphthalimide(0.43 g, 2.04 mmol) in heptane (50 mL) was heated under gentle reflux for 2 h, by which time an IR spectrum of an aliquot of the reaction mixture showed ν_{CO} bands from $PhCH_2Mn(CO)_5$ were absent. The mixture was evaporated to dryness and the residue was chromatographed on silica, with CH_2Cl_2/petroleum spirits (2:9) as eluent. Two yellow bands were resolved.

The slower moving band (R_f 0.15) was removed and recrystallized from CH_2Cl_2/petroleum spirits at −20 °C to give orange crystals of orthomanganated *N*-methyl-1,8-naphthalimide (**2**) (0.27 g, 40%). Anal.: Calc for $C_{17}H_8MnNO_6$: C 54.13; H 2.14; N 3.71%. Found C 54.44; H 2.21; N 3.66%. IR: ν(CO) cm^{-1} (CH_2Cl_2) 2086 m, 1999 vs, 1942 s; (KBr disc) 2083 s, 1995 vs, 1940 s, 1690 m, 1621 m, 1575 s, 1533 m. NMR ($CDCl_3$) ^1H: δ 3.55 s ($-CH_3$), 7.66 apparent t (dd),8.00 d, 8.23 d, 8.39 d, 8.48 d (all C–*H*). ^{13}C: δ 28.3 ($-CH_3$), 126.6, 132.1, 132.9, 136.3, 140.6 (all *C*–H), 120.3, 128.8, 130.4 (quart. *C*). ESI-MS (−ve ion, NaOMe added [16]): *m*/*z* 408.027, ($[M + OMe]^-$ calc. 407.991); (+ve ion): *m*/*z* 399.966 $[M + Na]^+$ calc. 399.962; *m*/*z* 776.936 $[2M + Na]^+$ calc. 776.936.

The faster moving band (R_f 0.60) was removed to give an orange powder of di-manganated *N*-methyl-1,8-naphthalimide (**3**) (0.05 g, 10%). Anal.: Calc for $C_{21}H_7Mn_2NO_{10}$ C 46.44; H 1.30; N 2.58%. Found C 47.98; H 1.84; N 2.54%. IR: ν(CO) cm^{-1} (CH_2Cl_2) 2084 m, 2002 vs, 1942 s; (KBr disc) 2086 s, 2012 w,sh, 1993 s, 1965 s, 1943 vs, 1613 s, 1606 sh. NMR ($CDCl_3$) ^1H: δ 3.56 s ($-CH_3$), 8.05 d, 8.32 d (both C–*H*). ^{13}C: δ 27.2 ($-CH_3$), 133.1, 137.9 (both *C*–H), 125.9, 126.8, 127.5 (quart. *C*) 176.4 (*C*=O), 204.0 (Mn–C), 210.5, 212.6, 220.9 (Mn–*C*O). ESI-MS (−ve ion, NaOMe added [16]): *m*/*z* 573.967, ($[M + OMe]^-$ calc 573.901).

2.4. Preparation of 2-(chloromercurio)-N-methyl-1,8-naphthalimide (**4**)

Cyclomanganated *N*-methyl-1,8-naphthalimide (0.030 g, 0.08 mmol) and $HgCl_2$ (0.033 g, 0.12 mmol) were dissolved in MeOH (10 mL) and heated to reflux for 75 min. The mixture was cooled and the precipitate was collected by filtration and washed with MeOH to give an off-white powder of 2-(chloromercurio)-*N*-methyl-1,8-naphthalimide (**4**) (0.030 g, 61%). Anal.: Calc for $C_{13}H_8ClHgNO_{12}$ C 34.99; H 1.81; N 3.14%. Found C 34.68; H 1.85; N 3.04%. IR: (KBr disk, cm^{-1}) 1698 m, 1643 vs, 1612 w, 1577 m. The compound was too insoluble for NMR spectra.

2.5. Preparation of 2-iodo-N-methyl-1,8-naphthalimide (**5**)

A solution of ICl (0.023 g, 0.14 mmol) in CCl_4 (1 mL) was added to **2** (0.05 g, 0.13 mmol) in CCl_4 (2 mL). The mixture was left for 2 h. Solvent was removed and the residue chromatographed on silica plates, eluting with CH_2Cl_2:petroleum spirits (1:1). A yellow band at R_f 0.3 was unreacted **2**, while a pale yellow band at R_f 0.1 was removed and shown to be the mono-iodinated product **5**, (4 mg, 9%). NMR ($CDCl_3$) ^1H: δ 3.61 s ($-CH_3$), 7.80 apparent t (dd), (J = 8 Hz), 7.80 d (J = 9 Hz), 8.21 dd (J = 8, 1 Hz), 8.38 d (J = 9 Hz), 8.69 dd (J = 7, 1 Hz) (all C–*H*); ^{13}C: 29.7 ($-CH_3$), 101.5, 126.9, 127.2, 131.2, 131.3, 131.5, 133.3, 133.9, 134.1, 141.7 (aryl *C*–H), 162.3, 163.2 (*C*=O). IR: (KBr disk, cm^{-1}) 1697 m, 1657 vs, 1646 sh, 1583 m. ESI-MS: *m*/*z* 359.952 $[M + Na]^+$, calc. 359.949; *m*/*z* 696.915 $[2M + Na]^+$, calc. 696.909. The structure of **5** was also determined by X-ray crystallography (see below).

2.6. Reaction of cyclomanganated N-methy-1,8-naphthalimide with phenylacetylene to give **6**

Cyclomanganated naphthalimide **2**, (0.040 g, 0.11 mmol) was dissolved in benzene (15 mL). PhCCH (0.1 mL, excess) was added and the stirred mixture was brought to reflux in an oil bath at 100 °C. After 90 min, a small sample removed for solution IR analysis showed all starting material was consumed. The solvent and excess alkyne were removed under vacuum and the residue chromatographed on silica plates, eluting with 1:1 CH_2Cl_2/pet spirits. This gave one major yellow band. This was removed and recrystallised from a mixture of CH_2Cl_2 and pet spirits to give orange crystals of **6** (0.044 g, 73%). Anal.: Calc for $C_{32}H_{20}MnNO_5$ C 69.45; H 3.64; N 2.52%. Found C 69.42; H 3.73; N 2.53%. IR: (CH_2Cl_2, cm^{-1}) 2019 s, 1954 s,br. NMR ($CDCl_3$) ^1H: δ 3.03 s ($-CH_3$), 5.60 s, 5.89 s (C–*H* of cyclohexadienyl ring), 5.94 d, 6.38 d (C–*H* of de-aromatised ring), 7.0–7.8 m, (aromatic C–*H*). ESI-MS: *m*/*z* 576.064 $[M + Na]^+$, calc. 576.061; *m*/*z* 1129.136 $[2M + Na]^+$, calc 1129.134.

2.7. X-ray crystal structures

Crystals of **2** and **5** were from CH_2Cl_2/Et_2O, while those of **6** were from CH_2Cl_2/petroleum spirits. Intensity data were obtained on a Bruker SMART diffractometer with Mo-Kα X-rays, and were corrected for absorption using a multi-scan procedure. The structures were solved by direct methods and developed and refined on F_o^2. For compound **2**, after the main part of the structure had been revealed it became clear there was disorder involving a 180° rotation of the planar naphthalimide rings relative to the $Mn(CO)_4$ group, giving an alternative orientation. This disordered component was resolved for all of the naphthalimide atoms and also for the Mn atom, and these were refined with isotropic temperature factors. The relative site occupancies were refined to give a major/minor orientation of 78%/22%. There was also concomitant disorder for the CO ligands but this was not resolved. H atoms were included in calculated positions for the major component but were omitted for the minor one. The structure of the main component is shown in Fig. 1a, with the disorder illustrated in Fig. 1b.

The crystal structure of **2** also appeared to have a minor (*ca* 3%) orientational disorder for one of the two independent molecules,

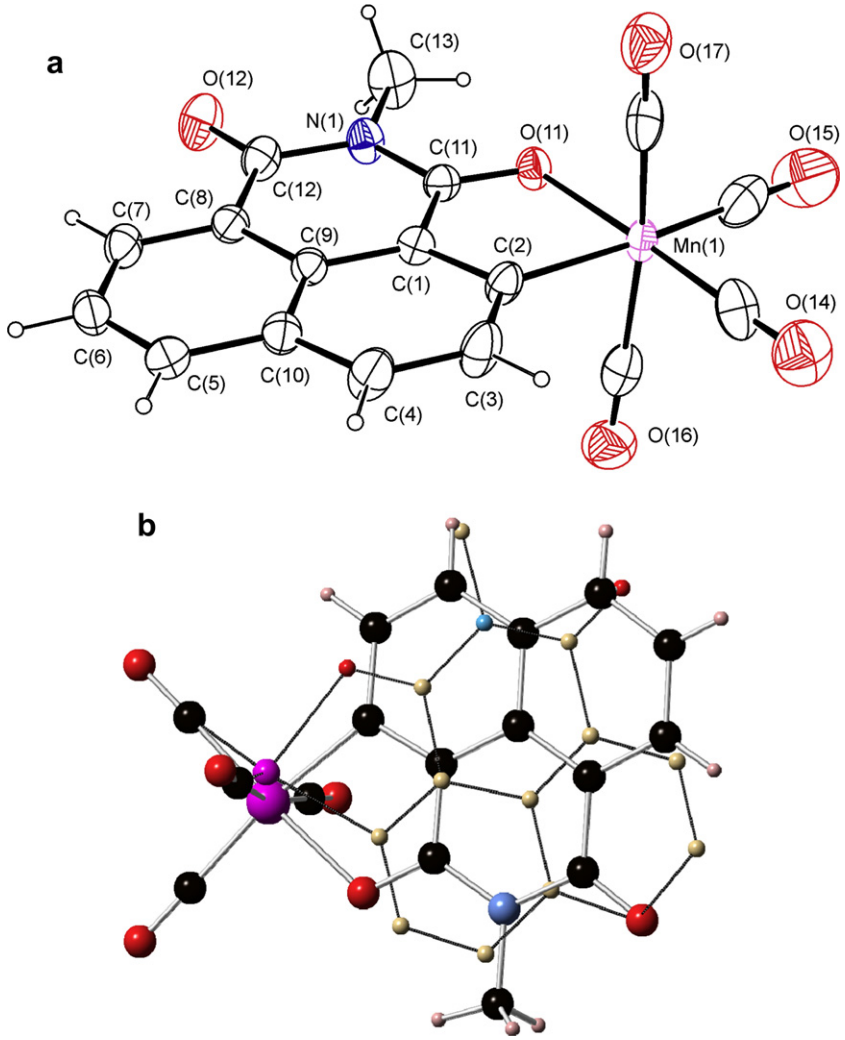


Fig. 1. a. The structure of the mono-manganated *N*-methyl-naphthalimide (**2**) with the disordered component omitted. b. A composite diagram showing the disorder found for the structure of **2**. The main component is shown with large spheres, the minor one with small ones.

showing a peak assignable to a fractional I atom on the opposite 2′-position, though other atoms associated with this small disorder were not apparent.

For **6** refinement was routine for the two independent molecules in the asymmetric unit and included all non-H atoms as anisotropic, with H atoms included in calculated positions.

All calculations were with the SHELX97 programs [18] run under WinGX [19]. Figures were generated with ORTEP-III [20] and with *Crystalmaker* [21]. Crystal and refinement details are given in Table 1 and the structures of **2**, **5** and **6** are illustrated in Figs. 1–3 respectively. Bond parameters are listed in the Supplementary information.

3. Results and discussion

3.1. Preparation of cyclomanganated complexes

When the *N*-methyl-1,8-naphthalimide **1** was heated under reflux with $PhCH_2Mn(CO)_5$ in heptane for 1.5–2 h (c.f. Ref. [9]) complete reaction occurred as monitored by the loss of the 2105 cm^{-1} ν_{CO} band of the starting complex, and appearance of the 2086 cm^{-1} band of the product, from infrared spectra on aliquots removed from the reaction mixture. Evaporation of the

Table 1
Crystal data and refinement details for the structure of **2**, **5** and **6**.

Formula	$C_{17}H_8MnNO_6$ (**2**)	$C_{13}H_8$ INO_2 (**5**)	$C_{32}H_{20}MnNO_5$ (**6**)
M_r	377.18	337.10	553.43
T(K)	89(2)	95(2)	93(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/n$	$P2_1/c$
a(Å)	7.1544(2)	7.9017(3)	17.3874(5)
b(Å)	9.4209(3)	16.3976(5)	12.8339(4)
c(Å)	12.4315(4)	16.9415(5)	22.6002(7)
α(°)	85.311(1)		
β(°)	77.482(1)	91.450(2)	90.295(2)
γ(°)	69.239(1)		
V(Å^3)	764.85(4)	2194.39(12)	5043.1(3)
Z	2	8	8
ρ(g cm^{-3})	1.638	2.041	1.458
μ(mm^{-1})	0.898	2.91	0.568
$T_{max,\ min}$	0.840, 0.758	1.000, 0.779	1.000, 0.860
Size (mm^3)	0.25 × 0.20 × 0.19	0.38 × 0.10 × 0.05	0.35 × 0.32 × 0.20
F(000)	380	1296	2272
θ_{max}(°)	28	28	28
Reflns collected	13,202	77,856	122,942
Unique reflns	3776 (R_{int} 0.034)	5225 (R_{int} 0.079)	12,111 (R_{int} 0.0547)
R_1 [$I > 2\sigma(I)$]	0.0479	0.0310	0.0336
wR_2 (all data)	0.1480	0.0724	0.0894
GOF on F^2	1.118	1.046	1.016

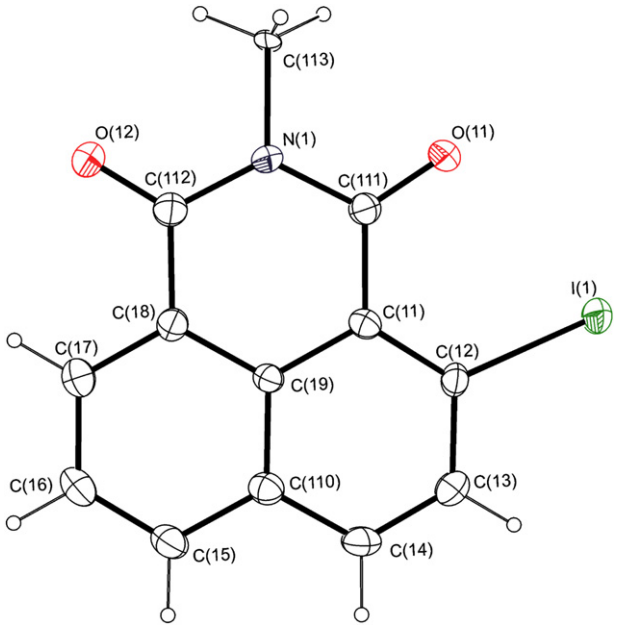


Fig. 2. The structure of one of the independent molecules of the iodinated product **5**.

solvent and chromatography of the residue on silica gave two major bands. The slower moving band was the mono-manganated compound **2**, as shown by microanalysis, high resolution ESI-MS, and by NMR and IR spectra. The IR spectrum contained the characteristic pattern for the $Mn(CO)_4$ group found near 2000 cm^{-1} in other cyclomanganated compounds, and also had a complicated set of bands at *ca* 1600 cm^{-1} arising from the free and coordinated C═O groups. The compound was also characterised by an X-ray structure analysis, the first for an ortho-manganated aryl amide. This is illustrated in Fig. 1 and shows the $Mn(CO)_4$ group is attached via a Mn–C bond at the 2-position on one of the aromatic rings, with the adjacent O of the amide making up the coordination sphere. Other than the two *trans* CO groups, the rest of the molecule is essentially planar, with none of the non-H atoms deviating from the least squares plane by more than 0.2 Å. Because of the disorder of the naphthalimide ligand a detailed comparison of bond parameters is not warranted, but the Mn–C and Mn–O bond distances [2.036(3) and 2.088(2) Å respectively] appear to be in the usual range for orthomanganated aryl ketones, as is the C(2)–Mn(1)–O(11) 'bite' angle of 80.5° [9]. The coordinated C═O is longer than the free one [1.256(3) vs 1.213(7) Å], consistent with the IR vibrational changes.

The faster moving band from the chromatography was shown to be the di-manganated species **3**. The NMR spectra reflected the symmetrical arrangement, as did the IR spectrum which together with ν_{CO} bands at the same positions as those of **2** for the metal carbonyl groups, also showed a simple pattern at *ca* 1600 cm^{-1} for the now-equivalent C═O groups, with frequencies lowered from those in the free naphthalimide arising from coordination to the Mn atoms.

The mono-substituted complex **2** was the major one formed when a 1:1 ratio of reactants was used, but the di-substituted was always a significant component from the reaction suggesting reactivity at one C═O group of **1** has little effect on the reactivity at the other C═O position. This behaviour is reminiscent of that observed with di-acetylbenzene as a substrate where both mono- and di-manganated compounds were formed with $PhCH_2Mn(CO)_5$ even at 1:1 ratios [10].

3.2. Reaction with $HgCl_2$

It has been shown that transmetalation of cyclomanganated arenes by Hg^{2+} occurs readily [22]. Accordingly when **2** was heated with $HgCl_2$ in MeOH, the corresponding 2-(chloromercurio) compound **4** was readily isolated in good yield and characterised.

The frequency of the C═O vibrations in the IR spectrum resemble those of a simple naphthalimide, suggesting only a weak, if any, interaction between the Hg and the adjacent O atom. This is as expected from related compounds that have been structurally characterised [23,24]. This ready synthesis of the mercury derivative of naphthalimide provides a substrate for the many different syntheses that are established based on aryl-mercury compounds [25], giving many potential 2-substituted naphthalimide compounds.

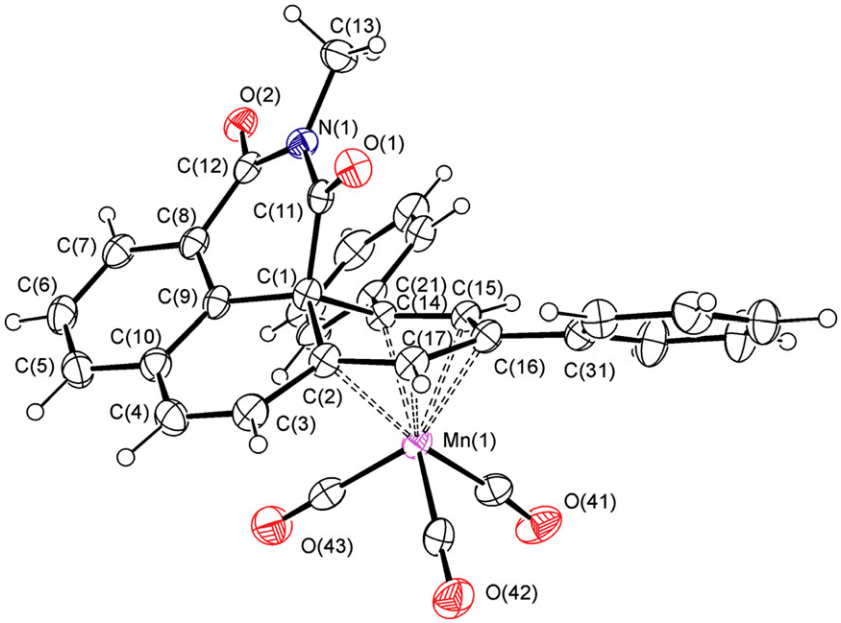
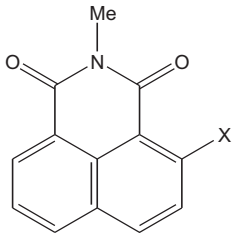


Fig. 3. A view of one of the independent molecules in the structure of **6** formed in the reaction of **2** with 2 mol of PhCCH.



(**4**) X = HgCl
(**5**) X = I

3.3. Reaction with ICl

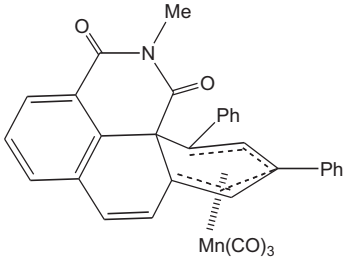
Cleavage of the Mn–C bond of orthomanganated arenes by halogens (Br_2 or ICl) is a useful way of generating aryl halides specifically *ortho* to an acyl group [26]. When **2** was reacted with ICl the reaction was less efficient than in earlier reported examples, leading to only low isolated yields (*ca* 10%) of the 2-iodonaphthalimide (**5**). This was characterised by spectroscopic means, and also by a single crystal structure, the first for a 2-substituted *N*-alkyl-1,8-naphthalimide. The structure is illustrated in Fig. 2 for one of the two independent molecules in the asymmetric unit. This shows the expected skeleton with an iodine atom at the 2-position. The molecule is essentially planar, though the I and O(1) atoms are twisted towards opposite sides (+0.49/−0.10 Å and +0.29/−0.25 Å respectively for molecules 1 and 2) presumably to reduce the steric interactions between these adjacent groups, giving I···O distances of 3.04 and 3.06 Å. This non-bonded steric interaction is also manifested in the C(1)–C(2)–I angle of 125° and C(1)–C(11)–O(1) of 124°. Compared with the structure of *N*-Et-1,8-naphthalimide [27] the ring C–C bonds adjacent to the iodo substituent are elongated. Molecules of **5** are stacked above each other with a ring-to-ring distance of 3.47 Å, very similar to the stacking in the unsubstituted *N*-Et-1,8-naphthalimide (3.45 Å).

Despite the limitation of low yield, this Mn–C cleavage reaction provides a direct route to 2-iodo-naphthalimides for further reactions in, for example, Heck coupling reactions and nucleophilic aromatic substitution chemistry.

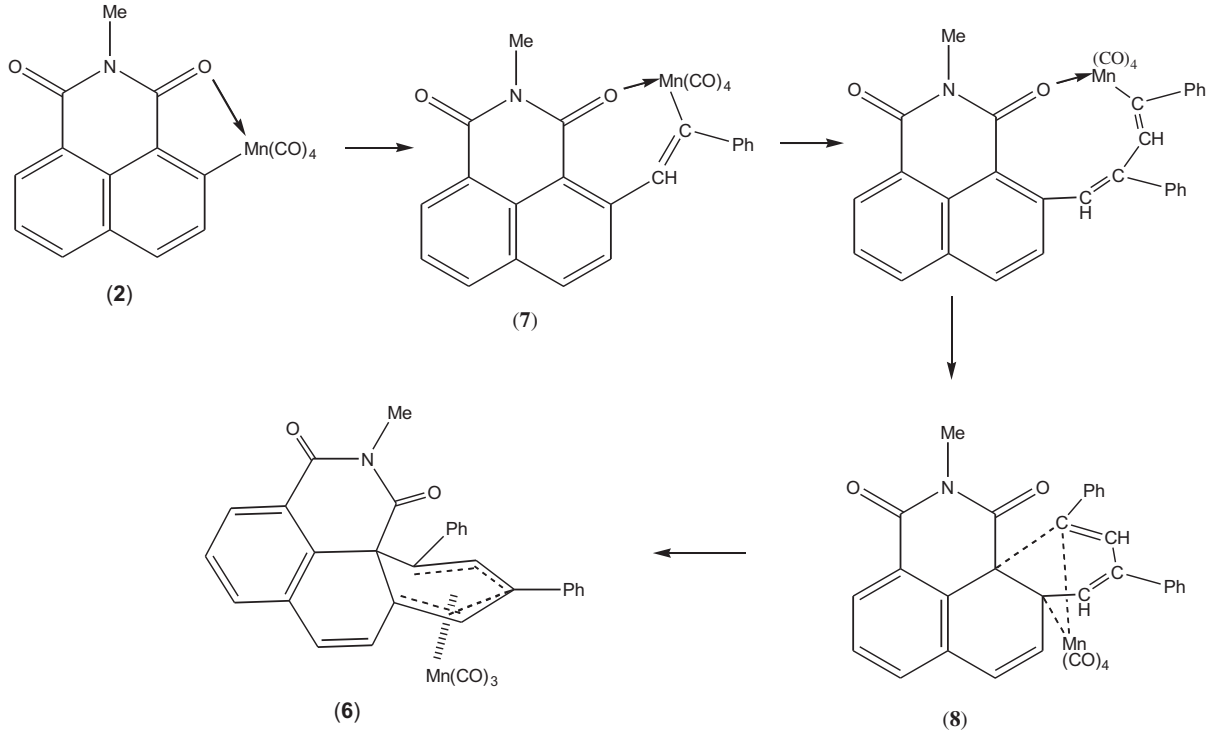
3.4. Reaction with PhCCH

Orthomanganated arenes are known to react readily with alkynes. For examples with acyl groups there is insertion into the Mn–C bond followed by a cyclisation reaction involving the acyl groups to form indenols and related species [14,15,28,29]. In the case of orthomanganated $P(OPh)_3$ or $Ph_3P{=}S$, insertion reactions with alkynes led to products with enlarged metallocyclic rings [30,31]. In other cases multiple insertions and cyclisations led to (η^5-cyclohexadienyl)$Mn(CO)_3$ compounds with the arene attached to the new ring [14].

When the cyclomanganated naphthalimide **2** was reacted with an excess of PhCCH a bright yellow compound was isolated in good yields. This contained the characteristic ν_{CO} bands of a $Mn(CO)_3$ group, and ESI-MS indicated that two equivalents of PhCCH had been added. Confirmation of the assignment as **6** came from a crystal structure determination. One of the two independent molecules in the asymmetric unit is illustrated in Fig. 3.



(**6**)



Scheme 1. A proposed mechanism for the formation of compound **6**.

Two molecules of PhCCH have coupled and added across the C_1–C_2 bond of the naphthalimide to generate a new six-membered ring, a cyclohexadienyl one to which a $Mn(CO)_3$ moiety is attached. This arrangement has surprisingly led to the de-aromatisation of the robust naphthalene ring of the imide. A possible mechanism is outlined in Scheme 1. Initial insertion of PhCCH would give the seven-membered ring in **7**. Based on the corresponding reaction of alkynes with cyclomanganated dialkylbenzamides [14] it would be expected that this would interact with the C=O bond to generate a new five-membered ring, but presumably the rigidity of the imide group in **2** prevents a suitable conformation for a similar process. Instead a second PhCCH inserts to give a larger ring. Transfer of the Mn from the O to the C_1–C_2 bond, as in **8** would encourage addition of the Mn–C bond across the C_1–C_2 "double" bond, with the $Mn(CO)_3$ group attaching to the face of the newly formed cyclohexadienyl ring.

As mentioned above, (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes have been found before in the reactions of orthomanganated arenes with alkynes [14]. However in all previous examples the cyclohexadienyl ring has been formed by trimerisation of three alkynes, the original aryl group ending up as a substituent on the new six-membered ring. It is not clear why a similar product was not produced in the present case, since an excess of PhCCH was used. The reaction is remarkably specific for **6**, with only very minor by-products.

The structure determination of **6** shows that the naphthalene unit of the molecule remains quite planar, despite the disruption of the aromaticity, with no atom displaced more than 0.23 Å, (molecule 1) or 0.13 Å (molecule 2) from the least squares planes through the ten C atoms. The imide group has twisted and is folded out of the naphthalene plane by *ca* 33°. The five C atoms of the cyclohexadienyl group which are bonded to Mn are coplanar to within ±0.05 Å, with Mn–C distances in the range 2.109–2.282 Å. The main difference between the two independent molecules of **6** is in the orientation of the two phenyl groups which form dihedral angles with the cyclohexadienyl plane of 31° and 37° for ring C(21)–C(26) and 25° and 39° for ring C(31)–C(36) respectively for molecules 1 and 2.

De-aromatisation of naphthalimides by addition reactions across the C_1–C_2 bond has been reported for photochemical reactions with alkenes or alkynes, leading to formation of cyclobutane or cyclobutene rings [32–34], but as far as we are aware there is no precedent for formation of a six-membered ring as in **6**, under relatively mild thermal conditions.

4. Conclusions

The efficient cyclomanganation of *N*-methyl-1,8-naphthalimide provides a means of specifically directing subsequent reactions to the 2-position. This has been demonstrated by simple cleavage of the Mn–C bond by $HgCl_2$ or ICl to give potentially useful substrates for further development. The reaction of the cyclomanganated complex with PhCCH follows an annulation route not observed previously for other manganated arenes, in forming a new six-membered ring fused to the naphthalene unit, thereby breaking the aromaticity.

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Appendix A. Supplementary material

CCDC 8844089–884091 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.jorganchem.2012.06.035.

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