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Cyclorhenated compounds derived from 1,4-diaryl-1-azabutadienes: preparation, structures and reactions

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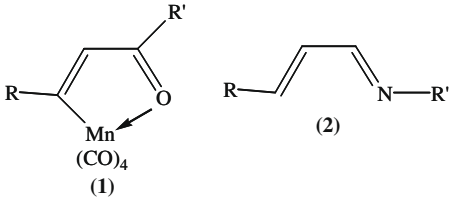
ABSTRACT

$PhCH_2Re(CO)_5$ reacted with 1,4-diaryl-1-azabutadienes to give cyclometallated (η^2-(C,N)-azabutadiene)$Re(CO)_4$ (**4**) together with the substituted derivatives (η^1-(N)-azabutadiene)(η^2-(C,N)-azabutadiene)$Re(CO)_3$ (**6** and **7**) The substituted product was shown by NMR and X-ray crystal structure analysis to be an inseparable mixture of isomers differing in the conformation of the η^1-ligand about the N=C bond—*trans* for (**6**) and *cis* for (**7**). Reaction of the mixture of **6** and **7** from 1,4-diphenyl-1-azabutadiene with phenyl acetylene gave η^5-(1,2,4-triphenyl-1-aza-cyclohexadienyl)$Re(CO)_3$.

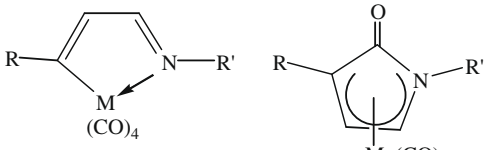
1. Introduction

Cyclometallation reactions are well-established for many of the metals in the periodic table, especially where the metallation has occurred at an aromatic carbon atom [1]. However examples involving cyclometallation of sp^2 carbon atoms from non-aromatic substrates are much less common. We have previously described the preparations of cyclomanganated species from enones (chalcones), **1**, and shown that their reactivity differs from that of cyclomanganated acyl-arenes [2]. As an extension of this work we investigated the manganese chemistry of related azabutadienes, **2** [3].



(1) (2)

Although we were unable to isolate the expected cyclomanganated compound **3**, it was assumed to be an intermediate for the final product of the reaction, the η^4-pyrrolinonyl complex **5**. It appears that first-formed **3** underwent spontaneous CO-insertion and cyclisation under the cyclometallation conditions. *In situ* reactions of the putative **3** as it formed, with alkynes or alkenes, gave products consistent with initial cyclomanganation [3]. Homrighausen et al. have reported some complexes of type **3** from an indirect route [4].



(**3** M = Mn)
(**4** M = Re)
(**5**)

Cyclorhenation reactions are comparatively unexplored [5], but we reasoned that the increased Re–C bond strength (compared to Mn–C) might slow CO-insertion so that the cyclorhenated azabutadiene **4** might be able to be isolated. This proved to be the case, though with some unanticipated complications, as detailed below.

2. Experimental

2.1. General

Solvents were dried and deoxygenated on a PureSolv PS-SD-5 purification system.

$PhCH_2Re(CO)_5$ was prepared from $PhCH_2Br$ and $Na[Re(CO)_5]$ as for $PhCH_2Mn(CO)_5$ [6]. The azabutadienes **2a–c** were prepared

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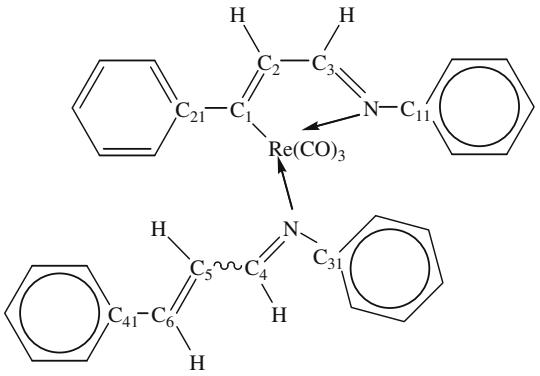
from the appropriate aromatic amines and cinnamaldehydes, using the method of Knolker [7], and were characterised by NMR and ESI-MS. ESI-MS were measured on a Fisons Platform II or a Bruker MicrOTOF spectrometer, using MeOH as solvent. NaOMe was added to aid ionisation [8]. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC300 or AC400 spectrometers using $CDCl_3$ as solvent. Assignments used standard DEPT, HSQC and HMBC procedures. Only selected data are given below, with full tables of assignments deposited as Supplementary material. The numbering system used for NMR assignments is:



2.2. Syntheses

2.2.1. General reaction of $PhCH_2Re(CO)_5$ with azabutadienes **2**

In a nitrogen-flushed Schlenk flask, the azabutadiene **2** (0.22 mmol) was added to a solution of $PhCH_2Re(CO)_5$ (94 mg, 0.23 mmol) in distilled heptane (20 mL). With continuous stirring, the clear yellow reaction solution was heated in an oil bath at 95–100 °C. As soon as the temperature reached 95 °C, the mixture turned red. Aliquots were removed for monitoring of ν_{CO} bands by infrared spectroscopy and the reaction was continued until the starting material was consumed (4–7 h). The resulting red solution with some red precipitate was cooled and the solvent was evaporated under vacuum. The residue was chromatographed on silica plates, eluting with CH_2Cl_2/petroleum spirits (2:3). This gave strong yellow and orange bands. These were extracted and crystallised separately from CH_2Cl_2/petroleum spirits at −20 °C, providing **4** as yellow, and **6/7** as red, crystals from the yellow and orange bands, respectively.

2.2.2. Characterisation of cyclorhenated compounds

*2.2.2.1. From the reaction with 1,4-diphenyl-1-azabutadiene **2a**.* Compound **4a**, yellow crystals, 29%, mp 169–171 °C. Anal. Calc. for $C_{19}H_{12}N_1O_4Re$: C, 45.23; H, 2.40; N, 2.78. Found: C, 45.45; H, 2.30; N, 2.87%. $\nu_{C\equiv O}$ (hexane) 2091 (w), 1990 (s), 1948 (m) cm^{-1}. NMR: ^{1}H (300 MHz, $CDCl_3$): δ 7.24 (d ^3J 2.26 Hz, H-2), 8.26 (d, ^3J 2.26 Hz, H-3); ^{13}C: 191.7 (CO *trans* to N), 191.1 (CO *trans* to C), 187.5 (*trans* COs), 218.5 (C-1), 177.9 (C-3), 137.0 (C-2). ESI-MS: (MeOH, +ve ion) *m/z* 505 $[M+H]^+$; (MeOH/NaOMe, −ve ion) *m/z* 535 $[M+OMe]^-$).

Compounds **6a/7a**, red crystals, 56%, [mixture of **6a** (as blocks) and **7a** (as needles) determined by X-ray crystallography, see below]. Anal. Calc. for $C_{33}H_{25}N_2O_3Re$: C, 57.97; H, 3.69; N, 4.10. Found: C, 57.23; H, 3.81; N, 3.97%. $\nu_{C\equiv O}$ (hexane) 2008 (s), 1913, 1897 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ (**6a**/**7a**, ratio *ca* 1.0:0.3) 6.25/6.87 (m, H-5), 6.98/6.98 (d ^3J 15.6 Hz, H-6), 7.28/7.10 (d, ^3J 2.3 Hz, H-2), 8.17/7.88 (d, ^3J 9.9 Hz, H-4), 8.40/8.15 (d, ^3J 2.3 Hz, H-3); ^{13}C NMR: δ (**6a**/**7a**) 200.7/200.1 (C-1), 176.3/176.0 (C-3), 171.8/174.6 (C-4), 147.6/150.4 (C-6), 135.3/135.9 (C-2), 120.7/122.7 (C-5). ESI-MS: (MeOH/NaOMe, +ve ion) *m/z* 707.137 ($[M+Na]^+$, $C_{33}H_{25}N_2NaO_3Re$, calcd. 707.132).

*2.2.2.2. From the reaction with 1-(p-fluorophenyl)-4-phenyl-1-azabutadiene **2b**.* Compound **4b**, yellow crystals, 15%, mp 145 °C. Anal. Calc. for $C_{19}H_{11}FN_1O_4Re$: C, 43.68; H, 2.12; N, 2.68. Found: C, 44.40; H, 2.13; N, 2.70%. $\nu_{C\equiv O}$ (CH_2Cl_2) 2092 (w), 1995 (s), 1983(vs), 1936 (m) cm^{-1}.

NMR: ^{1}H (300 MHz, $CDCl_3$): δ 7.23 (d ^3J 2.32 Hz, H-2), 8.23 (d, ^3J 2.32 Hz, H-3); ^{13}C: 191.4 (CO *trans* to N), 191.0 (CO *trans* to C), 187.4 (*trans* COs), 219.5 (C-1), 178.0 (C-3), 136.9 (C-2). ESI-MS: (MeOH/NaOMe, −ve ion) *m/z* 553 $[M+OMe]^-$.

Compounds **6b/7b**, red crystals (mixture of plates and needles), 77%. Anal. Calc. $C_{33}H_{23}F_2N_2O_3Re$: C, 55.07; H, 3.22; N, 3.89. Found: C, 55.07; H, 3.07; N, 3.91%. $\nu_{C\equiv O}$ (hexane) 2003 (s), 1899, 1892 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ (**6b**/**7b**, ratio *ca* 2:1) 6.25/7.11 (m, H-5), 7.00/7.00 (d, H-6), 7.25/7.08 (d, H-2), 8.15/7.86 (d, H-4), 8.35/8.11 (d, H-3); ^{13}C NMR: δ (**6b**/**7b**) 200.5/199.9 (C-1), 176.4/176.0 (C-3), 172.7/174.8 (C-4), 148.4/150.1 (C-6), 135.3/135.9 (C-2), 120.6/122.9 (C-5).

ESI-MS: (MeOH/NaOMe, +ve ion) *m/z* 742 ($[M+Na]^+$, (−ve ion) *m/z* 750 ($[M+OMe]^-$).

*2.2.2.3. From the reaction with 1-(p-tolyl)-4-(dimethylaminophenyl)-1-azabutadiene **2c**.* Compound **4c**, orange crystals, 32%, mp 210 °C. Anal. Calc. $C_{22}H_{19}N_2O_4Re$: C, 47.05; H, 3.41; N, 4.99. Found: C, 47.51; H, 3.53; N, 4.92%. $\nu_{C\equiv O}$ (CH_2Cl_2) 2089 (w), 1989 (s), 1974(s), 1926 (w) cm^{-1}. NMR: ^{1}H (300 MHz, $CDCl_3$): δ 7.25 (d ^3J 2.52 Hz, H-2), 8.16 (d, ^3J 2.52 Hz, H-3); ^{13}C: 192.6 (CO *trans* to N), 191.4 (CO *trans* to C), 188.2 (*trans* COs), 217.0 (C-1), 176.7 (C-3), 133.8 (C-2). ESI-MS: (MeOH/NaOMe, +ve ion) *m/z* 584 $[M+Na]^+$, 562 $[M+H]^+$; (−ve ion) *m/z* 592 $[M+OMe]^-$.

Compounds **6c/7c**, red crystals (mixture of blocks and needles), 77%. Anal. Calc. for $C_{39}H_{39}N_4O_3Re$: C, 58.70; H, 4.93; N, 7.02. Found: C, 58.88; H, 4.94; N, 7.01%. $\nu_{C\equiv O}$ (hexane) 2003 (s), 1899, 1892 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ (**6c**/**7c**, ratio *ca*1:2) 6.02/6.98 (m, H-5), 6.82/6.81 (d, H-6), 7.24/7.04 (d, H-2), 8.00/7.74 (d, H-4), 8.30/8.05 (d, H-3); ^{13}C NMR: δ (**6c**/**7c**) 201.8/201.1 (C-1), 175.1/174.6 (C-3), 171.7/174.1 (C-4), 147.7/150.3 (C-6), 132.1/132.7 (C-2), 116.1/123.7 (C-5).

ESI-MS: (MeOH/NaOMe, +ve ion) *m/z* 821.243 ($[M+Na]^+$, calcd. for $C_{39}H_{39}N_4NaO_3Re$ 821.243).

2.2.3. Reactions of cyclometallated **6a/7a**

2.2.3.1. With CO. A sample of the mixed isomers **6a** and **7a** was dissolved in CH_2Cl_2 and stirred for 24 h under an atmosphere of CO. An IR spectrum showed only bands arising from the starting complex, with no sign of the formation of any tetracarbonyl **4a**.

2.2.3.2. With p-methoxyphenyl isonitrile. p-Methoxyphenyl isonitrile (0.19 g 1.43 mmol) was added to a solution of **6a**/**7a** (0.19 g, 0.28 mmol) in heptane (15 mL). The mixture was heated in an oil bath at 100–105 °C for 5 h. After removal of solvent, the residue was chromatographed on silica plates, eluting with CH_2Cl_2/petroleum spirits (1:1). The main orange band (R_f 0.7) was collected and recrystallisation from CH_2Cl_2/petroleum spirits gave red crystals of the isonitrile derivative **8** (0.136 g, 80%). $\nu_{C\equiv O}$ (CH_2Cl_2) 2009 (s), 1939 (m), 1904 (m) cm^{-1}. NMR ($CDCl_3$): ^{1}H δ 7.20 (d ^3J 2.3 Hz) *H-2*; 8.27 (d ^3J 2.3 Hz) *H-3*. ^{13}C δ 135.6 (*C-2*); 176.3 (*C-3*); 225.2 (*C-1*). ESI-MS: (MeOH, +ve ion) *m/z* 632 $[M+Na]^+$; 610 $[M+H]^+$; (MeOH/NaOMe, −ve ion) *m/z* 640 $[M+OMe]^-$.

2.2.3.3. With phenyl acetylene. PhCCH (0.11 mL, 1.00 mmol) was added to a solution of **6a/7a** (0.21 g, 0.31 mmol) in heptane (15 mL). The mixture was heated in an oil bath at 95–100 °C for 2.5 h. Solvent was removed and the residue chromatographed with

CH_2Cl_2/petroleum spirits (7:5). The main yellow band (R_f 0.9) was removed and recrystallised from CH_2Cl_2/petroleum spirits to give yellow plates of the η^5-azacyclohexadienyl complex **9** (32 mg, 18%). $\nu_{C\equiv O}$ (CH_2Cl_2) 2026 (s), 1949 (m), 1935 (m) cm^{-1}. NMR ($CDCl_3$): ^1H δ 5.26 (d, ^3J 4.1 Hz) *H-4*; 5.83 (d ^3J 4.0 Hz) *H-5*; 6.63 (s) *H-7*. ^{13}C δ 57.2 (*C-4*); 93.9 (*C-5*); 101.0 (*C-6*); 90.7 (*C-7*); 79.8 (*C-8*). ESI-MS: (MeOH, +ve ion) *m/z* 601 $[M+Na]^+$; 308 $[M-Re(CO)_3]^+$; (MeOH/NaOMe, −ve ion) *m/z* 610 $[M+OMe]^-$, 578 $[M-H]^-$. The compound was fully characterised by an X-ray crystal structure determination.

2.3. X-ray crystallography

X-ray intensity data for compounds **4**a, **6a, 7a, 6b** and **9** were obtained from a Bruker APEX II CCD diffractometer, and were processed using standard software. Crystal data and refinement details are summarised in Table 1. Corrections for absorption were carried out using SADABS [9]. The structures were solved and refined using the SHELX programs [10], operating under WINGX [11]. All H atoms were included in calculated positions. Disorder of the C1/N1 atoms was possible for structures **4**, **6a** and **7a** with the 1,4-diphenylazabutadiene ligand, but in each case refinement with assignment of atom type reversed gave significantly higher *R* values and disparate U_{eq} values [e.g. for **6a** the U_{eq} values were N(1) 0.019 and C(1) 0.016 as assigned, N(1) 0.009 and C(1) 0.027 when reversed]. The ordered assignment was also supported from an analysis of the Re–CO distances, which consistently gave shorter values for those *trans* to N (average 1.927 Å) than those *trans* to C (average 1.952 Å) consistent with the different *trans*-influences.

3. Results and discussion

3.1. Reactions of $PhCH_2Re(CO)_5$ with 1,4-azabutadienes

The overall reactions are summarised in Scheme 1.

When a mixture of 1,4-diphenyl-1-azabutadiene and $PhCH_2Re(CO)_5$ was heated under reflux in heptane, the resulting red mixture provided two major products after chromatography. The first of these was yellow and was characterised as the cyclorhenated complex **4a**, the rhenium analogue of the implicated manganese metallocycle **3a** that could not be isolated in the previous investigation [3]. This was apparent from the microanalytical and mass spectrometry data, and also from the ν_{CO} bands which conformed to the usual pattern found for *cis*-$L_2M(CO)_4$ species. An X-ray crystal structure determination confirmed this assignment. As shown in Fig. 1 the azabutadiene has formed a five-membered cyclometallated group, coordinated through the N atom and the deprotonated C(1) atom.

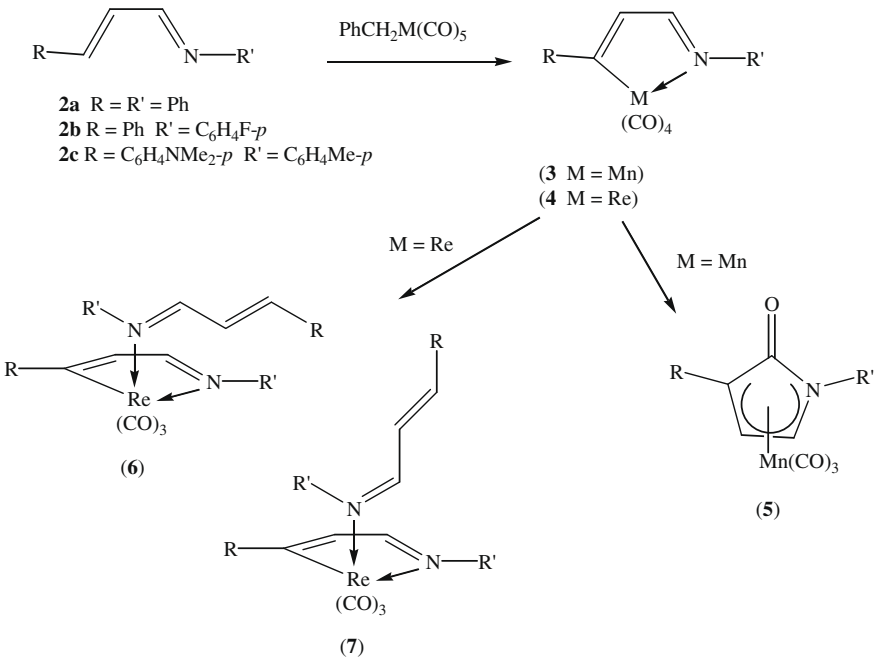
The ring is essentially planar, with the peripheral phenyl rings twisted out of the ring plane to avoid contact with the adjacent CO ligands. The Re–C and Re–N distances are essentially equal [2.188(2) and 2.185(2) Å], and are close to the values found in cyclorhenated species involving aryl metallation [5]. Coordination has increased the C(1)–C(2) and C(3)–N(1) distances, and decreased the C(2)–C(3) distance compared to the equivalent differences in uncomplexed azabutadienes, consistent with increased delocalisation around the metallocyclic ring. The Re–CO distances increase in the order Re–CO (*trans* to N(1)) > Re–CO (*trans* to C(1)) > Re–CO (*trans* to CO), reflecting the *trans* influence of the opposing species.

The second product of the reaction was intensely red. The crystallised material gave mass spectra and analytical data that indicated that *two* moles of the azabutadiene had been incorporated into the product, and the ν_{CO} bands were indicative of a *fac*-$Re(CO)_3$ group. A block-shaped crystal was selected and the structure was determined by X-ray crystallography as **6a**, as shown in Fig. 2a. The molecule is a derivative of the cyclometallated compound **4**, where one of the axial CO ligands has been replaced by a second azabutadiene group acting as a simple two-electron donor via the imine-N atom. This has had only a minor effect on the rest of the molecule with bond parameters of the metallocyclic ring essentially unchanged. The Re–N(2) distance of 2.238(2) Å is longer than Re–N(1), (2.186(2) Å), indicating a stronger coordination of the imine nitrogen when it is part of the metallocyclic ring.

The NMR data of the apparently pure red product were unexpectedly complicated and it was noted that the crystals were of two distinct forms – blocks and needles. Since the IR, elemental analysis and mass spectrometric data indicated a single compound it was initially assumed that these were polymorphs, however an X-ray determination on the needle crystals showed that it was actually a different isomer **7a**. This is illustrated in Fig. 2b, and differs in the geometry of the η^1-azabutadiene ligand about the C=N bond, which is *trans* for **6a** but *cis* for **7a**. This difference has had little effect on the parameters for the rest of the molecule. The Re–N(2) bond for the *cis* isomer, 2.188(2) Å, is shorter than the

Table 1
Crystal data and refinement details for **4a**, **6a**, **7a**, **6b** and **9**.

	4a	**6a**	**7a**	**6b**	**9**
Formula	$C_{19}H_{12}NO_4Re$	$C_{33}H_{25}N_2O_3Re$	$C_{33}H_{25}N_2O_3Re$	$C_{33}H_{23}F_2N_2O_3Re$	$C_{26}H_{18}NO_3Re$
M_r	504.50	683.75	683.75	719.73	578.61
T (K)	93(2)	84(2)	93(2)	97(2)	83(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbca	C2/c
a (Å)	12.4902(3)	12.0281(2)	9.3259(3)	13.8048(3)	22.3672(8)
b(Å)	17.5205(4)	14.4460(2)	10.0899(3)	14.8172(3)	10.9716(4)
c(Å)	8.1233(2)	15.7868(2)	29.4933(9)	27.0507(6)	17.0784(6)
β (°)	106.365(1)	97.690(1)	95.066(1)		93.127(1)
V (Å^3)	1705.64(7)	2718.41(7)	2764.40(15)	5533.2(2)	4184.9(3)
Z	4	4	4	8	8
D_c (g cm^{-3})	1.965	1.671	1.643	1.728	1.837
μ (mm^{-1})	7.15	4.51	4.43	4.44	5.84
Size (mm^3)	0.30 × 0.25 × 0.15	028 × 0.28 × 0.12	0.26 × 0.22 × 0.02	0.43 × 0.37 × 0.34	0.40 × 0.18 × 0.15
F (0 0 0)	960	1344	1040	2816	2240
θ_{max} (°)	35	26	34	28	32
Reflections collected	39 116	15 836	45 919	60 010	13 176
$T_{max,\ min}$	0.413, 0.223	0.413, 0.292	0.917, 0.392	0.313, 0.251	0.475, 0.204
Unique reflections	6436 (R_{int} 0.027)	5543 (R_{int} 0.024)	9871 (R_{int} 0.032)	6693 (R_{int} 0.0317)	6166 (R_{int} 0.0274)
Parameters	226	368	352	370	280
R_1 [$I > 2\sigma(I)$]	0.0163	0.0215	0.0312	0.0207	0.0273
wR_2 (all data)	0.0379	0.0530	0.0607	0.0549	0.0515
GOF on F^2	1.073	1.087	1.261	1.080	1.015



Scheme 1.

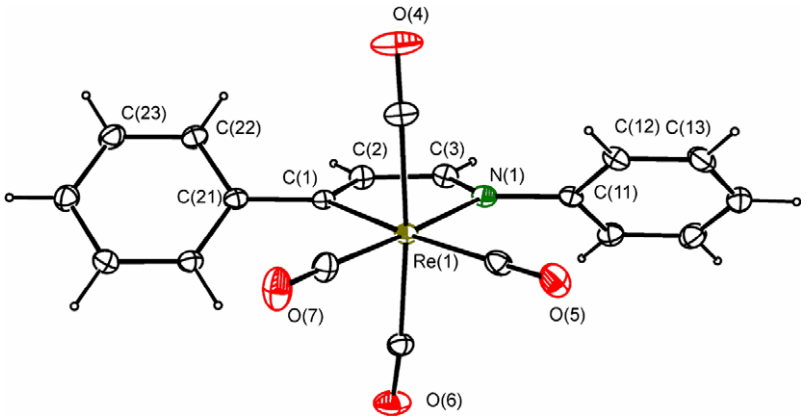


Fig. 1. The structure of the cyclometallated azabutadiene complex **4**. Selected bond lengths (Å): Re–C(1) 2.1877(16); Re–N(1) 2.1825(15); C(1)–C(2) 1.343(2); C(2)–C(3) 1.427(3); N(1)–C(3) 1.319(2).

Re–N(2) bond to the *trans*-η^1-azabutadiene in **6a**, 2.238(2) Å, suggesting a stronger donor bond in this case.

There appear to be no previous reports of a *cis*-azabutadiene acting as an η^1 ligand from amongst many studies describing η^1-*trans*-azabutadiene complexes [12]. The normal synthesis of azabutadienes gives >96% of the *trans* form [13], so the formation of significant amounts of **7a** in the reaction implicates a metal-induced isomerisation about the C=N bond. An NMR study of azabutadienes showed that lanthanide ions could induce *trans–cis* isomerisation, but no complexes were isolated [13]. The formation of a *cis* isomer for **7a** is presumably driven by steric factors; in **6a** the *trans*-geometry about the C=N bond directs the rest of the ligand so that it lies close to the substituents on the metallocyclic ring (Fig. 2a) whereas the *cis* geometry in **7a** allows the ligand to fold away from the rest of the complex (Fig. 2b).

Although the two isomers cannot be separated by chromatography, the relative amounts could be assessed from their NMR spectra. For the unsubstituted complex **4** the ^{1}H NMR spectrum shows two doublets at δ 7.24 and 8.26 ($^3J_{HH}$ = 2.26 Hz) which can be assigned to H-2 and H-3, respectively. In the spectra of the mixture of isomers there was one set of corresponding doublets at 7.28 and 8.40, and another at 7.10 and 8.15, with relative intensities *ca* 3:1. The sample used was made up of more block-shaped crystals than needles, so the more intense pair of doublets was assigned to the *trans* isomer **6a** and the latter pair to the *cis* one, **7a**. The two forms cannot be distinguished from their IR spectra, the ν_{CO} bands are not significantly different in spectra obtained from the distinct single crystal forms using a microscope attachment for the spectrometer.

The same reactions were carried out using the substituted aryl azabutadienes **2b** or **2c**. For reactions with a $PhCH_2Re(CO)_5$: azabutadiene ratio of 1:1, mixtures of the yellow cyclometallated-$Re(CO)_4$ complexes **4b** or **4c** with the red substituted $Re(CO)_3$ species **6b/7b** or **6c/7c** were obtained. The time needed for complete disappearance of the ν_{CO} bands of $PhCH_2Re(CO)_5$ was approximately seven hours for **2b** but only three hours for **2c**. This is possibly because of the effects of the electron-withdrawing F versus the electron-releasing Me on the basicity of the N atom, but more examples would be needed to be sure this was the main contributor.

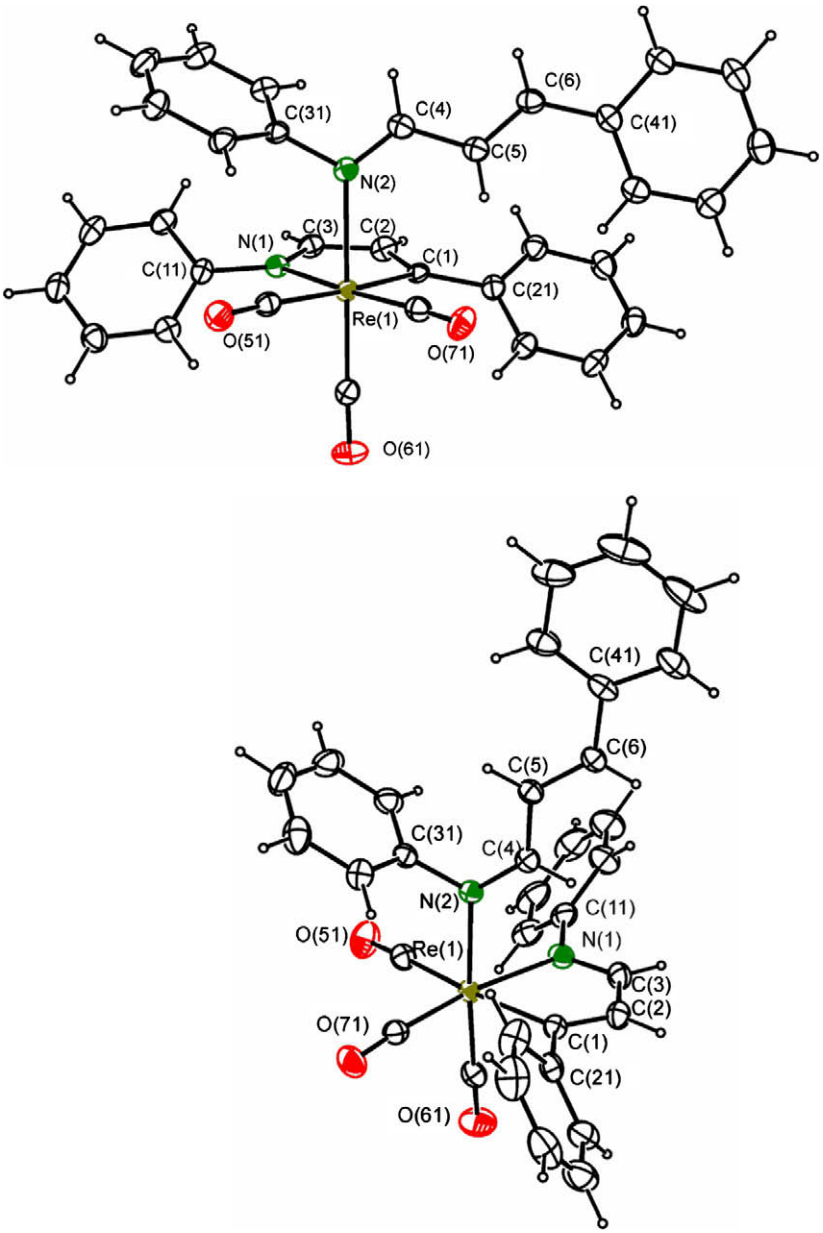


Fig. 2. The two isomers of the substituted complex, with *trans* (**6a**) and *cis* (**6b**) η^1-azabutadiene ligands. Selected bond lengths (Å) for **6a** [**6b**] are: Re–C(1) 2.187(3) [2.178(2)]; Re–N(1) 2.186(2) [2.183(2)]; Re–N(2) 2.238(2) [2.188(2)]; C(1)–C(2) 1.352(4) [1.346(4)]; C(2)–C(3) 1.423(4) [1.423(4)]; C(4)–C(5) 1.437(4) 1.443(3)]; C(5)–C(6) 1.342(4) [1.341(3)]; N(1)–C(3) 1.313(4) [1.315(4)]; N(2)–C(4) 1.295(4) [1.294(3)].

Recrystallisation of the red compounds again gave two distinct forms of crystals for the substituted compounds, and a complex ^{1}H NMR spectrum, showing that two isomers were also being formed with these azabutadienes. An X-ray crystal structure analysis of a block-shaped crystal from the reaction with the *p*-fluorophenyl azabutadiene showed it was the *trans* isomer **6b**, so the needles that co-formed were assumed to be the *cis* form, as with the unsubstituted species. The structure of **6b** is illustrated in Fig. 3 and confirms that it is a direct analogue of **6a**. The presence of the fluoro group has no significant effect on the structural parameters, with even the relative conformations of the aryl rings being such that the two structures are essentially superimposable despite being in different space groups with different crystal packing interactions.

For **6b**/**7b** and **6c**/**7c** the ^{1}H NMR spectra could be used to distinguish the two isomers, by comparison with the chemical shifts for the H-2, H-3, H-4 and H-5 protons established for **6a**/**7a**. For the *trans* isomers the H-3 and H-2 signals of the cyclometallated azabutadiene were doublets at 8.30–8.40 and 7.24–7.28, respectively, with $^3J_{HH}$ coupling of 2.2–2.4 Hz, while for the *cis* isomers these signals were ~0.2 ppm upfield at 8.05–8.15 and 7.04–7.10 ppm, respectively. For the η^1-azabutadiene, the H-4 signal was 8.00–8.17 for the *trans* isomers and 7.74–7.86 for the *cis* ones with $^3J_{HH}$ ~10 Hz. The largest difference was for H-5 which was 6.02–6.24 for the *trans* isomers and 6.87–7.11 for the *cis*. ^{13}C shifts were less useful for distinguishing the two forms, with the largest difference being for C-5 which appeared at 116–120 ppm for the *trans* and ~123 ppm for the *cis* forms.

Interestingly, the NMR data indicated that the *trans* isomers **6a** or **6b** were favoured over **7a** or **7b**, but that the *cis* form **7c** dominated over *trans* **6c** with the methyl-substituted azabutadiene, possibly indicating a more facile isomerisation of azabutadiene **2c**.

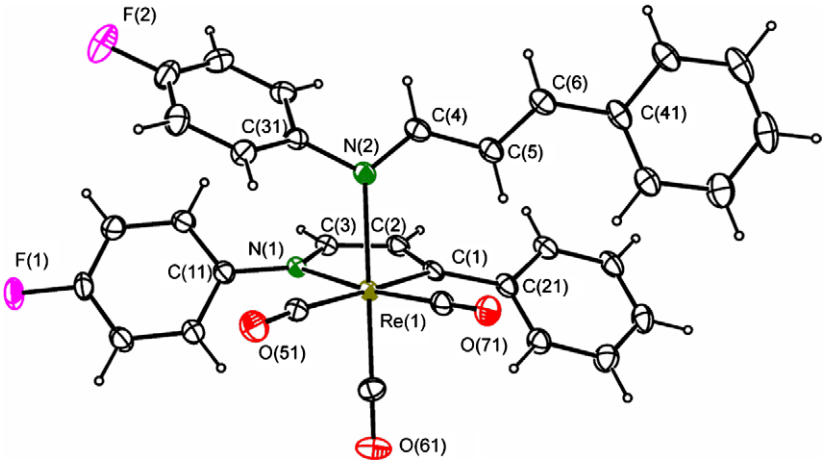
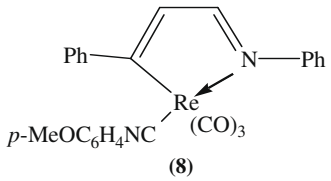


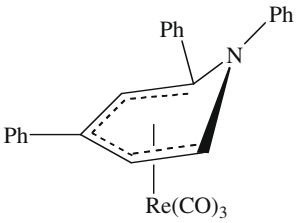
Fig. 3. The structure of **6b**. Bond lengths (Å) include: Re–C(1) 2.183(2); Re–N(1) 2.186(2); Re–N(2) 2.238(2).

3.2. Some reactions of the cyclorhenated complexes

Attempts were made to displace the η^1-azabutadiene ligand from **6a/7a**. When a solution was stirred under one atmosphere of CO for 24 h there was no change observed. However with *p*-methoxyphenyl isonitrile, displacement of the ligand was observed in heptane at *ca* 100 °C, giving the substituted cyclorhenated species **8** in reasonable yield.



(8)



(9)

The reaction of **6a/7a** with phenyl acetylene was investigated. This led to the isolation of an η^5-azacyclohexadienyl-rhenium complex **9**, which was structurally characterised since no azacyclohexadienyl examples have been described before for rhenium. The structure is illustrated in Fig. 4. The crystals are isomorphous with the manganese example reported earlier [3]. The C(4)–C(8) atoms are essentially planar, forming a dihedral angle with the C(4)–N(1)–C(8) plane of 48.7° (50° for the Mn analogue). The Re–C distances range from 2.271 to 2.344 Å with an average of 2.304 Å, 0.16 Å longer than the average for the manganese compound (2.146 Å). The difference between the average M–CO bonds is 0.13 Å for the Re and Mn analogues, so bonding appears very similar in the two species with the differences arising simply from the increased atomic radius. When compared with a (cyclohexadienyl)$Re(CO)_3$ complex [14], the average Re–C_{ring} bonds are 0.033 Å shorter, and the Re–CO bonds are 0.062 Å longer, for the azacyclohexadienyl

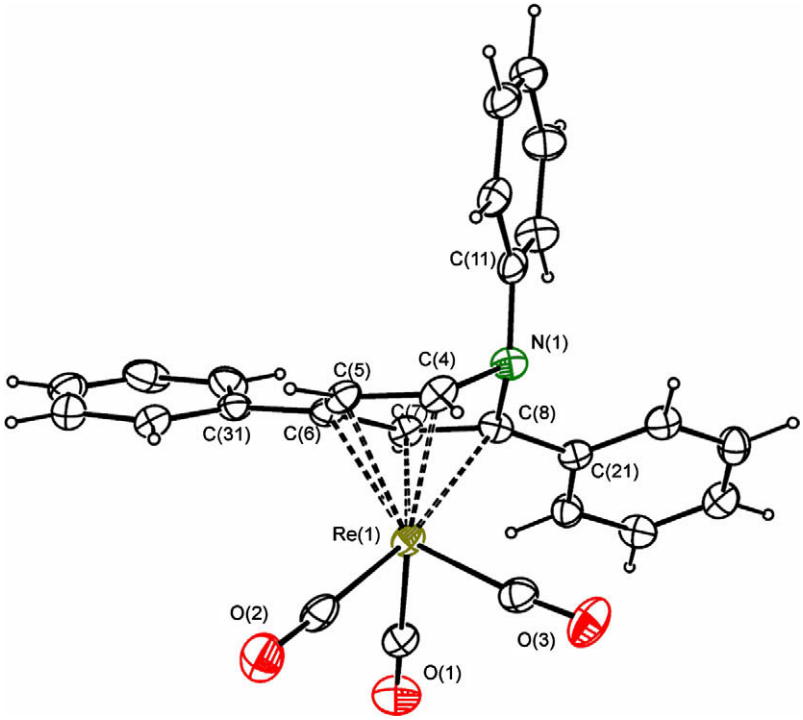


Fig. 4. The structure of **9**. Selected bond lengths (Å): Re–C(4) 2.298(3); Re–C(5) 2.271(3); Re–C(6) 2.329(3); Re–C(7) 2.276(3); Re–C(8) 2.344(3); N(1)–C(4) 1.450(4); N(1)–C(8) 1.462(3); N(1)–C(11) 1.417(4).

complex **9**, suggesting the heterocyclic ring is a better π-acceptor ligand.

The manganese analogue of **9** was prepared from an *in situ* reaction of $PhCH_2Mn(CO)_5$, diphenylazabutadiene and PhCCH and was assumed to involve the intermediacy of the cyclometallated compound **1**, which was not directly observed [3]. The isolation of the rhenium complex **9** from a cyclometallated precursor under comparable conditions supports this previously suggested pathway.

3.3. Summary

In none of the reactions examined was there any indication that the rhenium system was forming the analogue of the manganese compound **5**, nor in the earlier investigation of the manganese system [3] was there any evidence for compounds of type **6a/7a**. Hence in this system there is a very clear distinction in the reactivities for the manganese and rhenium reagents. It is probable that in both cases the reaction initially gives the cyclometallated tetracarbonyl species **3** or **4,** respectively, for manganese and rhenium. For **3** there is rapid CO-insertion into the Mn–C bond followed by rearrangement, a process which is not observed at all for the rhenium analogue; this is understandable since insertion reactions into a strong Re–C bond are generally more sluggish than those into a weaker Mn–C bond. What is more surprising is the ease with which one of the CO ligands in the rhenium case **4** is replaced by another molecule of azabutadiene. This is obviously facile since it occurs extensively even when there is a deficit of azabutadiene relative to $PhCH_2Re(CO)_5$, suggesting the remaining CO ligands are labilised by the formation of the cyclometallated ring. However this is not seen with the manganese example despite the fact that substitution reactions are usually more readily performed with manganese rather than rhenium carbonyls. An additional surprise was the apparent ability of the rhenium complex to induce *cis–trans* isomerism about the N=C bond in the azabutadiene.

Acknowledgements

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Appendix A. Supplementary material

CCDC 742573, 742574, 742575, 742576 and 742577 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.033.

References

[1] M.I. Bruce, Angew. Chem., Int. Ed. 16 (1977) 73;
L. Main, B.K. Nicholson, Adv. Metal-Org. Chem. 3 (1994) 1;
A.D. Ryabov, Chem. Rev. 90 (1990) 403;
I. Omae, Coord. Chem. Rev. 248 (2004) 995.
[2] W. Tully, L. Main, B.K. Nicholson, J. Organometal. Chem. 503 (1995) 75;
W. Tully, L. Main, B.K. Nicholson, J. Organometal. Chem. 507 (1996) 103;
W. Tully, L. Main, B.K. Nicholson, J. Organometal. Chem. 633 (2001) 162.
[3] W.J. Mace, L. Main, B.K. Nicholson, D.J. van de Pas, J. Organometal. Chem. 689 (2004) 2523.
[4] C.L. Homrighausen, J.J. Alexander, J.A. Krause Bauer, Inorg. Chim. Acta 334 (2002) 419.
[5] R.J. McKinney, R. Hoxmeier, H.D. Kaesz, J. Am. Chem. Soc. 97 (1975) 3059;
H. Preut, H.J. Haupt, Acta Crystallogr., Sect. A 36 (1980) 1196;
M.A. Guillevic, M.E. Light, S.J. Coles, T. Gelbrich, M.B. Hursthouse, D.W. Bruce, Dalton Trans. (2000) 1437;
M.A. Leeson, B.K. Nicholson, M.R. Olsen, J. Organometal. Chem. 579 (1999) 243;
S. Choua, J.-P. Gjukic, J. Dallery, A. Bieber, R. Welter, J.-P. Gisselbrecht, P. Turek, L. Ricard, Inorg. Chem. 48 (2009) 149.
[6] M.I. Bruce, M.J. Liddell, G.N. Pain, Inorg. Synth. 26 (1989) 172.
[7] H.J. Knölker, G. Baum, N. Foitzik, H. Goesmann, P. Gonser, P.G. Jones, H. Röttele, Eur. J. Inorg. Chem. (1998) 993.
[8] W. Henderson, J.S. McIndoe, B.K. Nicholson, P.J. Dyson, J. Chem. Soc., Dalton Trans. (1998) 519.
[9] R.H. Blessing, Acta Crystallogr., Sect. A51 (1995) 33.
[10] G.M. Sheldrick, SHELX97 Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[11] (a) L.J. Farrugia, WINGX, Version 1.70.01, University of Glasgow, UK.;
(b) L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[12] L. Stamp, H.T. Dieck, Inorg. Chim. Acta 147 (1988) 199;
C. Muller, L. Stamp, H.T. Dieck, J. Organometal. Chem. 308 (1986) 105;
D. Walther, S. Gessler, U. Ritter, A. Schmidt, K. Hamza, W. Imhof, H. Goris, J. Sieler, Chem. Ber. 128 (1995) 281;
A.N. Nesmeyanov, L.V. Rybin, N.A. Steizer, Y.T. Struchkov, A.S. Batsanov, M.I. Rybinskaya, J. Organometal. Chem. 182 (1979) 399.
[13] J.M.A. Al-Rawi, L.M.N. Saleem, Spectrosc. Lett. 24 (1991) 161.
[14] C. Lowe, V. Shklover, H.W. Bosch, H. Berke, Chem. Ber. 126 (1993) 1769.