Journal of Organometallic Chemistry 695 (2010) 96–102

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

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ARTICLE INFO

Article history:
Received 31 July 2009
Received in revised form 21 September 2009
Accepted 24 September 2009
Available online 3 October 2009

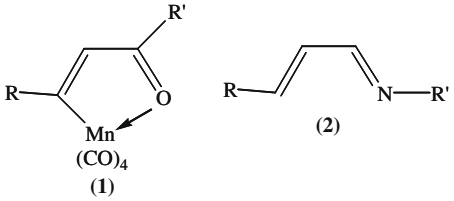
Keywords:
Cyclometallation
Rhenium
Azabutadiene
Cis/*trans* isomerisation
Crystal structures
Azacyclohexadienyl

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)$Re(CO)_3$.

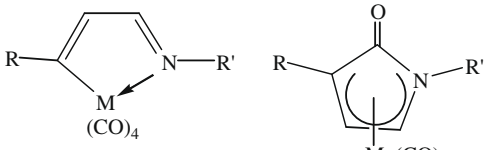
1. Introduction

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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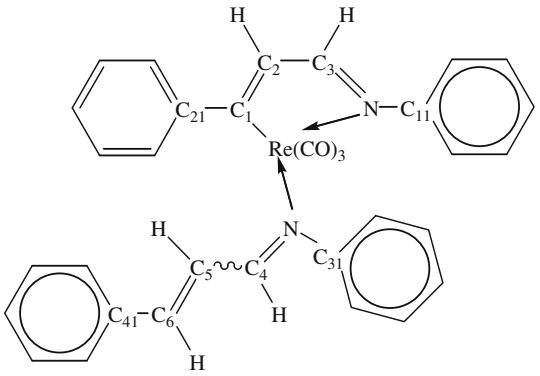
doi:10.1016/j.jorganchem.2009.09.033

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