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Insertion of NH into the rhenium–carbon bonds of a Fischer-type rhenacyclobutadiene. Preparation and characterization of azarhenacyclic complexes

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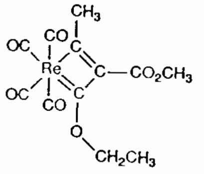
Abstract

The rhenacyclobutadiene complex $(CO)_4\overline{ReC(CH_3)C(CO_2CH_3)C}(OEt)$ (**1**) reacts with 2,4-dinitrophenylhydrazine, tosylhydrazine or hydrazine hydrochloride to afford a new five-membered azarhenacyclic complex, $(CO)_4\overline{ReNHC(CH_3)C(CO_2CH_3)C}(OEt)$ (**4**), as a stable yellow solid. **4** was characterized by elemental analysis, EI mass spectrometry and IR and ^1H and ^{13}C NMR spectroscopy, and its structure was elucidated by X-ray diffraction techniques. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.721(1)$, $b = 12.172(2)$, $c = 15.013(2)$ Å, $\alpha = 86.42(1)$, $\beta = 88.83(1)$, $\gamma = 79.48(1)°$, and four molecules per unit cell. The five-membered azarhenacycle is essentially planar, and the bond distances in the ring indicate strong electron delocalization, similar to that of the reported [1] analogous oxarhenacyclic complex $(CO)_4\overline{ReOC(CH_3)C(CO_2CH_3)C}(OEt)$ (**2**). Reaction between **1** and hydrazine monohydrate yields a mixture of **4** (minor product) and isomeric $(CO)_4\overline{ReC(CH_3)C(CO_2CH_3)C(OEt)NH}$ (major product, **5**). The structure of **5** was assigned from spectroscopic evidence. **4** and **5** may be considered as organometallic analogues of pyrrole, i.e. rhenapyrrole complexes. Reaction of **4** with LDA followed by quenching with DCl in D_2O at *c.* −78 °C results in hydrogen–deuterium exchange at the nitrogen atom.

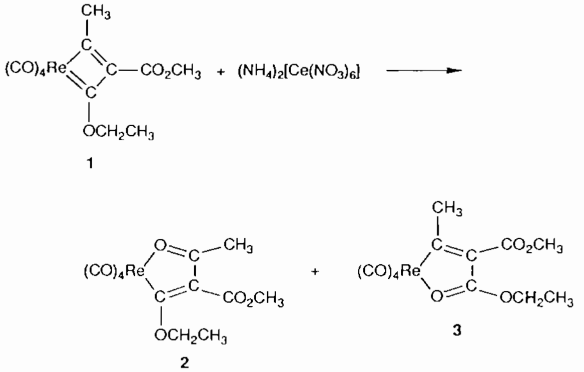
Key words: Crystal structures; Rhenium complexes; Azarhenacycle complexes

Introduction

We have recently reported in detail our studies on the synthesis, structure and reaction chemistry of the novel Fischer-type rhenacyclobutadiene complexes, $(CO)_4\overline{ReC(R)C(CO_2CH_3)C}(OEt)$ (R = H, CH_3 (**1**), CO_2CH_3) [1]. The chemistry of **1** in nucleophilic addition/substitution and oxidation reactions closely parallels that of Fischer carbene complexes [2]. For example, treatment of **1** with $(NH_4)_2[Ce(NO_3)_6]$ affords the oxygen atom insertion products **2** and **3** (eqn. (1)) [1]. A similar oxidation reaction occurs with Fischer carbene complexes [2a, 3] as illustrated in eqn. (2).



1



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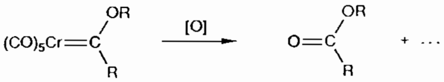

(2)

Since the NH fragment is isoelectronic with the oxygen atom, we considered an extension of the insertion chemistry of **1** (eqn. (1)) to reaction with NH. Insertion reactions of NH into the M=C bond of Fischer carbene complexes have been reported. Examples are provided

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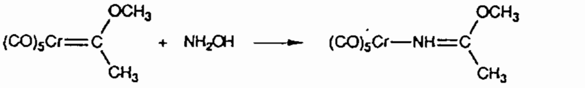
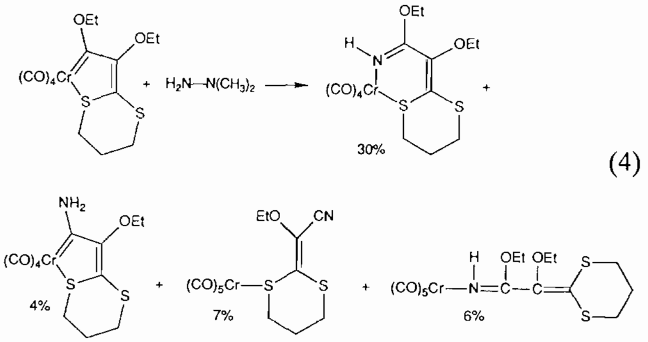
by reactions of such complexes with hydroxylamine (eqn. (3)) [4] and *S*,*S*-diphenylsulfilimine, $NH{=}SPh_2$ [5].



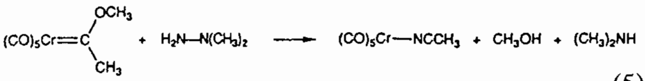
$$(CO)_5Cr{=}C(OCH_3)(CH_3) + NH_2OH \longrightarrow (CO)_5Cr{-}NH{=}C(OCH_3)(CH_3) \quad (3)$$

The use of 1,1-disubstituted hydrazines also affords an NH group insertion product when a bidentate carbene complex of chromium is employed (eqn. (4)) [6];



(4)

however, with a simple metal carbene, only a nitrile complex results (eqn. (5), M = Cr, W) [4].



$$(CO)_5Cr{=}C(OCH_3)(CH_3) + H_2N{-}N(CH_3)_2 \longrightarrow (CO)_5Cr{-}NCCH_3 + CH_3OH + (CH_3)_2NH \quad (5)$$

In this paper, we report the synthesis and characterization of novel five-membered azarhenacyclic complexes obtained by insertion of the NH fragment into the Re=C bonds of the rhenacyclobutadiene ring of **1**.

Experimental

General procedures and measurements

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of Ar using standard procedures [7]. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. IR, NMR (^{1}H, ^{2}H and ^{13}C), and mass spectra (EI) were obtained as previously described [1].

Materials

All solvents were purified by distillation under an Ar atmosphere prior to use. Hexane (a mixture of hexanes), THF and CH_2Cl_2 were distilled from Na/K alloy, potassium benzophenone ketyl and CaH_2, respectively.

Reagents were obtained from various commercial sources and used as received, except as noted below. Literature procedures were used to synthesize $(CO)_4\overline{ReC(CH_3)C(CO_2CH_3)C}(OEt)$ (**1**) [1] and tosylhydrazine [8].

Preparation of $(CO)_4\overline{ReNHC(CH_3)C(CO_2CH_3)C}(OEt)$ *(4)*

Method 1. A solution of **1** (150 mg, 0.33 mmol) and 2,4-dinitrophenylhydrazine (65 mg, 0.33 mmol) in 15 ml of THF was stirred at room temperature for 2 days. The solvent was then removed under reduced pressure, the residue was treated with 20 ml of hexane, and the resulting suspension was stirred overnight. The mixture was filtered to remove an orange solid, and the filtrate was evaporated to dryness to afford yellow crystalline **4** (140 mg) in 90% yield. Further purification can be effected by chromatography on alumina (6% H_2O) eluting with 1:1 CH_2Cl_2/hexane. IR (hexane): ν(NH) 3350 (w-m br), ν(CO) 2095 (w), 1994 (vs), 1943 (s), 1695 (m br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.8 (s, br, NH), 4.41 (q, J = 7.1 Hz, CH_2CH_3), 3.74 (s, CO_2CH_3), 2.38 (d, J = 0.3 Hz, CCH_3), 1.46 (t, J = 7.1 Hz, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 239.3 (s, *C*OEt), 191.7, 190.9 (2s, *cis* COs), 190.4 (s, CCH_3), 185.8 (s, *trans* COs), 166.3 (s, CO_2CH_3), 124.3 (s, CCO_2CH_3), 67.8 (t, OCH_2CH_3), 51.0 (q, CO_2CH_3), 26.2 (q, CCH_3), 15.6 (q, OCH_2CH_3). MS (EI), ^{187}Re isotope: *m/z* 468.95 (M^+), 441 ($M^+ - CO$), 411.93 ($M^+ - 2CO - H$), 384 ($M^+ - 3CO - H$), 356 ($M^+ - 4CO - H$), 325 ($M^+ - 4CO - H - OCH_3$). *Anal.* Calc. for $C_{12}H_{12}NO_7Re$: C, 30.77; H, 2.58; N, 2.99. Found: C, 31.00; H, 2.39; N, 2.93%.

Method 2. A solution of **1** (312 mg, 0.69 mmol) and 1 equiv. of tosylhydrazine (128 mg) in 20 ml of THF was stirred at room temperature for 2 days. A work-up similar to that in method 1 followed to give a comparable yield of **4**.

Preparation of $(CO)_4\overline{ReC(CH_3)C(CO_2CH_3)C(OEt)N}H$ *(5)*

To a solution of **1** (105 mg, 0.23 mmol) in 10 ml of THF at 0 °C was added 1 equiv. of hydrazine monohydrate (11 μl). The resulting solution was allowed to warm to room temperature and was stirred overnight. The solvent was then evaporated, and the residue was dissolved in *c.* 1 ml of CH_2Cl_2. To this solution was added a layer of hexane (20 ml). After 2 h, the colored supernatant solution was separated from the solid residue. A ^{1}H NMR spectrum of this solution showed the presence of **5** and a small amount of **4**. Purification of **5** was effected by removal of the solvent and stirring the residual oil in 20 ml of hexane at 0 °C. A white solid separated from the green solution and was dried for several hours *in vacuo*, yield 28 mg (26%). IR (hexane): ν(NH) 3390 (w br), ν(CO) 2090 (w), 1990 (s), 1935 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.9 (s br, NH), 4.13 (q, J = 7.0 Hz, OCH_2CH_3), 3.79 (s, CO_2CH_3), 2.82

(s, CCH_3), 1.43 (t, $J=7.0$ Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$) δ 212.9 (s, CCH_3), 191.3, 191.0 (2s, *cis* COs), 186.7 (s, *trans* COs), 179.6 (s, COEt), 166.2 (s, CO_2CH_3), 131.5 (CCO_2CH_3), 62.6 (t, OCH_2CH_3), 51.4 (q, CO_2CH_3), 33.8 (q, CCH_3), 13.7 (q, OCH_2CH_3). MS (EI), ^{187}Re isotope: m/z 469 (M^+), 441 (M^+-CO), 413 (M^+-2CO), 385 (M^+-3CO), 357 (M^+-4CO), 325 ($M^+-4CO-H-OCH_3$). *Anal.* Calc. for $C_{12}H_{12}NO_7Re$: C, 30.77; H, 2.58. Found: C, 30.84; H, 2.71%.

Deuteration of $(CO)_4\overline{ReNHC(CH_3)C(CO_2CH_3)C}(OEt)$ *(4)*

A solution of **4** (50 mg, 0.11 mmol) in 5 ml of THF at −78 °C was treated with 1 equiv. of LDA (75 μl, 1.5 M solution) in cyclohexane. The mixture was stirred for 30 min as its color turned from yellow to brown, and then the reaction was quenched by addition of a solution of DCl in D_2O (20% by wt., 99.5% D), all at low temperature. Almost immediately the original yellow color reappeared. After 30 min of additional reaction time the solvent was evaporated and the solid residue was extracted with hexane. Filtration of the hexane extract and removal of the solvent from the filtrate afforded a yellow–green solid. IR (hexane): ν(CO) 2095 (w), 1994 (vs), 1943 (s), 1695 (m br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.41 (q, $J=7.1$ Hz, CH_2CH_3), 3.74 (s, CO_2CH_3), 2.38 (s, CCH_3), 1.46 (t, $J=7.1$ Hz, CH_2CH_3). ^2H NMR (CH_2Cl_2): δ 6.98 (s, ND).

Crystallographic analysis of $(CO)_4\overline{ReNHC(CH_3)C(CO_2CH_3)C}(OEt)$ *(4)*

Crystals of **4** suitable for an X-ray diffraction study were obtained by slow evaporation of solvent from a CH_2Cl_2 solution of **4** saturated with hexane. The data collection crystal was a yellow–gold plate with well-formed faces. Examination of the diffraction pattern on a Rigaku AFC5S diffractometer indicated a triclinic crystal system so that the space group is restricted to $P1$ or $P\bar{1}$. The cell constants were determined by a least-squares fit of the diffractometer setting angles for 25 reflections in the 2θ range 28–30° with Mo Kα radiation ($\lambda(K\bar{\alpha})=0.71073$ Å).

The intensities of six standard reflections, which were measured after every 150 reflections, decreased slightly during the course of data collection. The average change in intensity was 5.3%, and a linear decay correction was applied to the data. An analytical absorption correction was also applied to the data [9].

The structure was solved by using the Patterson method in SHELXS86 in space group $P\bar{1}$ [10]. There are two molecules in the asymmetric unit, and these are labeled as A and B. The two Re atoms were located on the Patterson map, and the rest of each molecule was elucidated by standard Fourier methods. Full-matrix least-squares refinements were done in TEXSAN [11]; the function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with $w=1/\sigma^2(F_o)$. The hydrogen atoms bonded to carbon atoms were included in the model as fixed contributions in calculated positions with C–H = 0.98 Å and $B_H=1.2B_{eq}$ (attached carbon atom). The methyl hydrogen atoms were idealized to sp^3 geometry based on positions located in various difference electron density maps. The set of methyl hydrogen atoms bonded to C(4A) has two orientations, and each is included in the model with occupancy factors set to 0.5. The same is true for the set of methyl hydrogen atoms bonded to C(6B). The hydrogen atoms bonded to nitrogen atoms were initially located on a difference electron density map, and then added to the model and refined isotropically.

The final refinement cycle for the 5120 reflections with $F_o^2>\sigma(F_o^2)$ and the 387 variables resulted in agreement indices of $R=0.031$ and $R_w=0.032$. The maximum and minimum peaks in the final difference electron density map are 0.90 and −0.82 e/Å^3. Scattering factors for the non-hydrogen atoms [12a] and the hydrogen atoms [12b] were used and included terms for anomalous scattering for the former [12a].

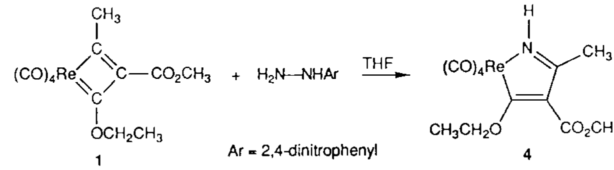
Further crystallographic details are provided in Table 1. Final positional and equivalent isotropic thermal parameters are given in Table 2.

Results and discussion

Reactions of the rhenacyclobutadiene complex 1 with hydrazines

In looking for a reagent that would provide an NH fragment for insertion into one of the Re=C bonds of **1**, we initially considered using monosubstituted hydrazines that contain a good amino leaving group. We thought that such a leaving group would favor N–N bond cleavage necessary for the insertion. Our first choice of hydrazine was 2,4-dinitrophenylhydrazine.

Reaction of **1** with 2,4-dinitrophenylhydrazine proceeds cleanly at room temperature to afford, within 2 days, complete conversion to a single rhenium-containing product, **4**, derived by insertion of NH into the Re=C(CH_3) bond (eqn. (6)). A proposed mechanism for this reaction is presented in Scheme 1 and



1

Ar = 2,4-dinitrophenyl

4

(6)

TABLE 1. Crystallographic data for **4**

Formula	$C_{12}H_{12}NO_7Re$
Formula weight	468.44
Space group	$P\bar{1}$
a (Å)	8.721(1)
b (Å)	12.172(2)
c (Å)	15.013(2)
α (°)	86.42(1)
β (°)	88.83(1)
γ (°)	79.48(1)
V (Å^3)	1563.7(4)
Z	4
D_{calc} (g cm^{-3})	1.99
Crystal size (mm)	$0.11\times0.29\times0.38$
Radiation	Mo Kα with graphite monochromator
μ (cm^{-1})	79.03
Transmission factors	0.17–0.44
Temperature	ambient
2θ Limits (°)	$4\leqslant2\theta\leqslant55$
Scan speed	4° min in ω with max. 4 scans reflection^{-1}
Scan type	ω–2θ
Scan range (° in ω)	$1.30+0.35\tan\theta$
Data collected	$+h$, $\pm k$, $\pm l$
Unique data	7185
Unique data ($F_o^2>\sigma(F_o^2)$)	5120
No. variables	387
$R(F)$	0.031
$R_w(F)$	0.032
Error in obsn of unit weight	1.13

TABLE 2. Positional and equivalent isotropic thermal parameters for **4**

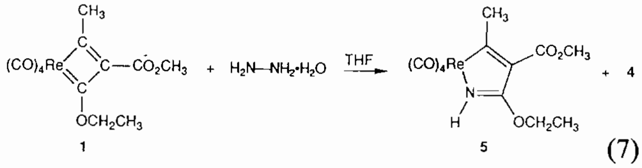
Atom	x	y	z	B_{eq}[a] (Å^2)
Re(1A)	0.14812(3)	0.21122(2)	0.42805(2)	4.41(2)
O(1A)	0.4172(5)	0.4900(4)	0.2095(3)	6.4(3)
O(2A)	0.5883(5)	0.3923(4)	0.3034(3)	5.7(3)
O(3A)	0.4343(5)	0.3404(4)	0.4492(3)	5.3(3)
O(4A)	0.1907(7)	0.1488(5)	0.6287(3)	7.3(4)
O(5A)	−0.1316(9)	0.0861(6)	0.4240(4)	9.6(5)
O(6A)	−0.0953(7)	0.4234(5)	0.4728(4)	7.1(4)
O(7A)	0.391(1)	−0.0010(6)	0.3879(5)	11.9(6)
N(1A)	0.1274(6)	0.2591(5)	0.2889(3)	4.3(3)
C(1A)	0.2196(7)	0.3202(5)	0.2519(3)	3.5(3)
C(2A)	0.3360(7)	0.3496(5)	0.3079(3)	3.5(3)
C(3A)	0.3288(7)	0.3101(5)	0.3967(4)	3.9(3)
C(4A)	0.2031(7)	0.3542(6)	0.1546(4)	4.6(4)
C(5A)	0.4448(7)	0.4183(5)	0.2686(4)	3.9(3)
C(6A)	0.7018(8)	0.4553(7)	0.2672(5)	6.6(5)
C(7A)	0.443(1)	0.3038(8)	0.5437(4)	7.2(6)
C(8A)	0.579(1)	0.334(1)	0.5802(5)	10.0(8)
C(9A)	0.177(1)	0.1734(6)	0.5543(5)	5.5(4)
C(10A)	−0.027(1)	0.1293(7)	0.4263(5)	6.4(5)
C(11A)	−0.0042(9)	0.3484(6)	0.4560(4)	4.9(4)
C(12A)	0.301(1)	0.0757(8)	0.4027(5)	7.0(6)
Re(1B)	0.97175(3)	0.72629(2)	0.14178(1)	3.54(1)
O(1B)	1.1104(6)	0.8121(5)	−0.1836(3)	6.3(3)
O(2B)	1.3229(5)	0.8501(4)	−0.1278(3)	5.2(3)
O(3B)	0.9052(4)	0.8760(3)	−0.0440(2)	4.0(2)
O(4B)	0.6276(6)	0.8113(5)	0.1881(3)	6.8(3)
O(5B)	1.0152(7)	0.5848(5)	0.3210(3)	7.5(4)
O(6B)	0.8453(6)	0.5369(4)	0.0527(3)	5.8(3)
O(7B)	1.0600(8)	0.9286(5)	0.2369(4)	8.4(4)
N(1B)	1.2098(6)	0.6699(5)	0.1059(3)	4.2(3)
C(1B)	1.2630(6)	0.7021(5)	0.0287(4)	3.7(3)
C(2B)	1.1510(6)	0.7740(5)	−0.0278(3)	3.3(3)
C(3B)	1.0040(6)	0.8046(5)	0.0094(3)	3.2(3)
C(4B)	1.4293(7)	0.6627(6)	0.0024(4)	5.1(4)
C(5B)	1.1893(6)	0.8127(5)	−0.1202(4)	3.6(3)
C(6B)	1.3664(9)	0.8855(7)	−0.2170(5)	6.0(5)
C(7B)	0.7481(7)	0.9172(6)	−0.0149(4)	4.6(4)
C(8B)	0.6741(8)	0.9975(7)	−0.0859(5)	6.0(4)
C(9B)	0.7570(8)	0.7812(6)	0.1702(4)	4.8(4)
C(10B)	0.9972(8)	0.6377(6)	0.2553(4)	4.7(4)
C(11B)	0.8978(7)	0.6047(6)	0.0843(4)	4.2(3)
C(12B)	1.0308(8)	0.8559(6)	0.2010(4)	5.2(4)

[a] The form of the equivalent isotropic displacement parameter is: $B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a^*_ia^*_j\mathbf{a}_i\cdot\mathbf{a}_j$.

consists of the following steps: (i) attack of the hydrazine at the electrophilic Re=C(CH$_3$) carbene carbon atom to give a zwitterionic intermediate, (ii) proton migration from the NH$_2$ to the NH nitrogen atom, (iii) nucleophilic attack of Re at NH with displacement of ArNH$_2$, (iv) cleavage of the Re–C(CH$_3$) bond to yield the five-membered ring-expansion product. This sequence of steps represents an adaptation of a similar mechanism suggested by Raubenheimer *et al.* [5] for the insertion of the NH group of NH=SPh$_2$ into the M=C bond of Fischer carbene complexes.

Complex **4** also forms in the reactions of **1** with other electron poor hydrazines, viz. tosylhydrazine and hydrazine hydrochloride. In the latter case, the reaction proceeds more slowly, probably owing to low solubility of hydrazine hydrochloride. Thus, after 24 h of reaction time at the reflux temperature of THF, only slightly more than 50% conversion was realized.

The reaction of **1** with the more electron rich hydrazine monohydrate affords a mixture of **4** and the isomeric azarhenacycle **5** (eqn. (7)). The major product **5** was purified by extraction into hexane at 0 °C to remove a small amount of **4**. In contrast, the structurally analogous oxarhenacycles **2** and **3** (cf. eqn. (1)) could not be separated [1].



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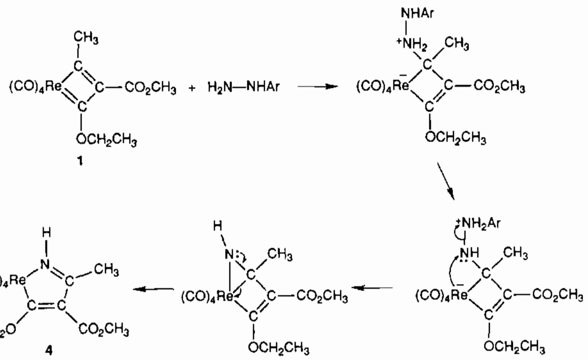
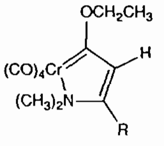
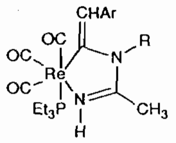


Scheme 1.

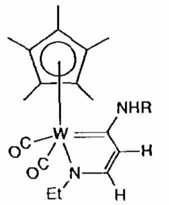
Only a limited number of five-membered azametallacycles have been prepared. For example, de Meijere and co-workers [13] reported the synthesis and characterization of azachromacycles **A**, which were obtained as intermediates in the preparation of highly substituted cyclopentadienes. Alexander and co-workers [14] synthesized a series of azarhenacycles **B** by thermal reactions of $(CO)_4Re(CH_2C_6H_4X\text{-}p)(CNR)$ (X = Cl, OCH_3, R = $p\text{-}C_6H_4CH_3$, 2,6-xylyl) with PEt_3 in acetonitrile. Filippou *et al.* [15] achieved selective synthesis of the azametallacycles **C** by reaction of a tungsten η^3-1-azaallyl complex with alkyl isocyanides. Although insertion of NH has received considerable recent attention [5, 16], to our knowledge, no five-membered azametallacycles had been obtained by such a ring-expansion reaction starting with hydrazines.



A



B



C

*Characterization of the azarhenacyclic complexes **4** and **5***

Complexes **4** and **5** are yellow and white air-stable solids, respectively. Their composition was established by elemental analysis and EI mass spectrometry. The structures of these isomeric azarhenacyclic complexes were inferred from their IR and ^{1}H and ^{13}C NMR spectra. An X-ray diffraction analysis of **4** was performed to confirm the spectroscopically deduced structure and to compare it with that of the analogous oxarhenacycle **2** [1].

Crystals of **4** contain two crystallographically independent molecules A and B that differ in the orientation of the CO_2CH_3 substituent at C(2). The structure of molecule A is shown in Fig. 1. The CO_2CH_3 group participates in intermolecular hydrogen bonding with the N atom, the distances N(1B)···O(1A) and N(1A)···O(1B) being 2.955(7) and 2.917(7) Å, respectively.

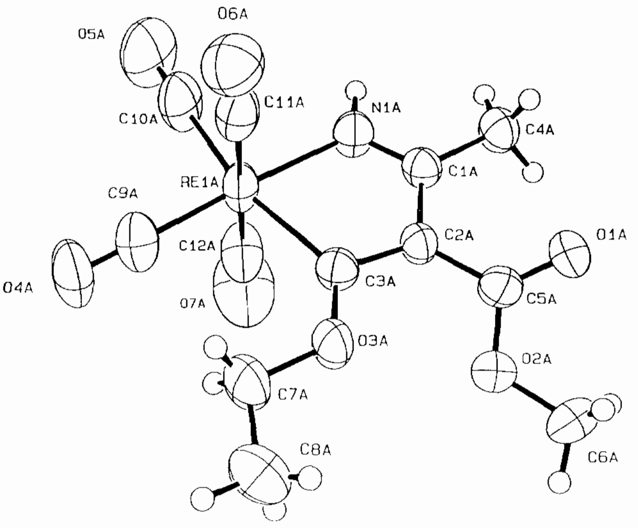
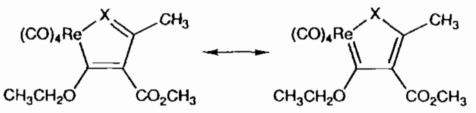


Fig. 1. ORTEP drawing of molecule A of **4**. The non-hydrogen atoms are represented by 50% probability thermal ellipsoids. The hydrogen atoms are drawn with an artificial radius.

Selected bond distances and angles of molecules A and B are listed in Table 3. Both molecules contain a five-membered azarhenacyclic ring, with the NH group being bonded to the metal and the CCH_3 carbon atom. Thus, insertion of NH occurred into the $Re{=}C(CH_3)$ bond of the rhenacyclobutadiene complex **1**. The azarhenacyclic ring is essentially planar, with C(1A) being displaced 0.02 Å from the 'best' four-atom plane N(1A)–Re(1A)–C(3A)–C(2A) in molecule A, and C(2B) being 0.05 Å away from the 'best' four-atom plane C(1B)–N(1B)–Re(1B)–C(3B) in molecule B. For comparison, the oxarhenacyclic ring of **2** adopts more of an envelope conformation that places the Re atom 0.16 Å from the plane of one oxygen and three carbon atoms.

The bond distances within the respective rings of **4** (average distances) and **2** [1] are given in Fig. 2. The values of the carbon–carbon distances indicate extensive electron delocalization in the chelate ring, which may be described in terms of contributions of resonance structures **I** and **II** (X = NH or O). Structure **I** appears to have gained importance compared to structure **II** on going from the oxarhenacyclic ring to the azarhenacyclic ring.



I II

TABLE 3. Selected bond distances (Å) and angles (°) for **4**

Re(1A)–N(1A)	2.136(5)	Re(1B)–N(1B)	2.133(5)
Re(1A)–C(3A)	2.178(6)	Re(1B)–C(3B)	2.185(5)
O(1A)–C(5A)	1.201(7)	O(1B)–C(5B)	1.188(6)
O(2A)–C(5A)	1.342(7)	O(2B)–C(5B)	1.326(7)
O(2A)–C(6A)	1.437(8)	O(2B)–C(6B)	1.446(7)
O(3A)–C(3A)	1.339(7)	O(3B)–C(3B)	1.345(6)
O(3A)–C(7A)	1.459(7)	O(3B)–C(7B)	1.440(6)
N(1A)–C(1A)	1.287(7)	N(1B)–C(1B)	1.304(7)
C(1A)–C(2A)	1.439(7)	C(1B)–C(2B)	1.438(7)
C(1A)–C(4A)	1.496(7)	C(1B)–C(4B)	1.495(8)
C(2A)–C(3A)	1.394(7)	C(2B)–C(3B)	1.385(7)
C(2A)–C(5A)	1.467(8)	C(2B)–C(5B)	1.488(7)
N(1A)–Re(1A)–C(3A)	73.9(2)	N(1B)–Re(1B)–C(3B)	73.9(2)
Re(1A)–N(1A)–C(1A)	119.7(4)	Re(1B)–N(1B)–C(1B)	120.0(4)
N(1A)–C(1A)–C(2A)	116.8(5)	N(1B)–C(1B)–C(2B)	115.5(5)
N(1A)–C(1A)–C(4A)	119.2(5)	N(1B)–C(1B)–C(4B)	120.6(5)
C(2A)–C(1A)–C(4A)	124.0(5)	C(2B)–C(1B)–C(4B)	123.9(5)
C(1A)–C(2A)–C(3A)	114.3(5)	C(1B)–C(2B)–C(3B)	115.4(5)
C(1A)–C(2A)–C(5A)	118.8(5)	C(1B)–C(2B)–C(5B)	122.6(5)
C(3A)–C(2A)–C(5A)	126.9(5)	C(3B)–C(2B)–C(5B)	122.0(5)
Re(1A)–C(3A)–O(3A)	130.6(4)	Re(1B)–C(3B)–O(3B)	131.6(4)
Re(1A)–C(3A)–C(2A)	115.3(4)	Re(1B)–C(3B)–C(2B)	115.0(4)
O(3A)–C(3A)–C(2A)	114.1(5)	O(3B)–C(3B)–C(2B)	113.4(4)

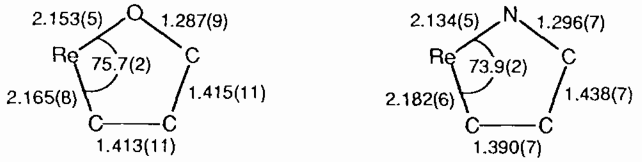
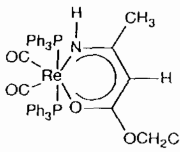


Fig. 2. Salient metrical data for the metallacyclic rings of **2** (left) and **4** (right).

The Re–C(3) bond distance of 2.182(6) Å (av.) in **4** represents an intermediate value between Re–C$_{sp^2}$ single (*c.* 2.22 Å) and double (*c.* 2.09 Å) bonds [17]. The Re–N bond length of 2.134(5) Å (av.) is similar to the bond distances of 2.145(3) Å in a delocalized six-membered ring of **D** [18] and 2.146(4) Å in a non-delocalized five-membered ring of **B** (Ar = *p*-$C_6H_4OCH_3$, R = 2,6-xylyl) [14]. The value of the C(1)–N bond distance (1.296(7) Å (av.) is closer to that of a C=N double bond (typically 1.27 Å) than a C–N single bond (typically 1.44 Å) [19]. The sum of bond angles around the nitrogen center of 360° points to sp^2 hybridization at this atom. All of these data underscore the importance of resonance structure **I** (X = NH) for the azarhenacycle **4**.



D

Spectroscopic data of **4**, presented in 'Experimental', show remarkable similarities to those of **2** [1], except for effects of replacement of oxygen with an NH group. Thus, in the ^{1}H NMR spectrum of **4**, the signal of the CCH_3 protons is observed at δ 2.38, exactly as for **2**. However, for the azarhenacycle, this signal occurs as a doublet (J = 0.3 Hz) owing to spin–spin coupling with the NH hydrogen, which resonates at δ 6.8 (s br). Irradiation at the frequency of the latter signal collapses the doublet CH_3 resonance to a singlet. The presence of an NH group in **4** is also evidenced by the appearance of a broad IR ν(NH) absorption at 3350 cm^{-1} [20].

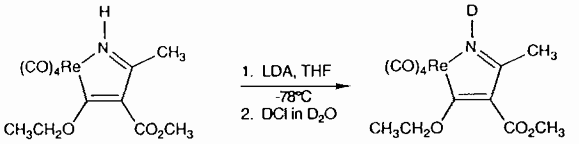
The ^{13}C NMR spectrum of **4** closely resembles that of **2**. For example, the signal of the *C*OEt carbon occurs at δ 239.3 for **4** and δ 258.5 for **2**, reflecting a substantial amount of carbenoid character of this atom in each complex. The resonance of the *C*CH_3 carbon is observed at δ 190.4 for **4** and δ 211.8 for **2**, being shifted upfield from its position for **1** at δ 246.4. The chemical shifts of each of the *C*CO_2CH_3 and C*C*O_2CH_3 carbon atoms are almost identical for the two rhenacycles.

Complex **5** has been assigned an isomeric azarhenacyclic structure derived by NH group insertion into the Re=C(OEt) bond of **1** from ^{1}H and ^{13}C NMR data. Again, these data show striking similarities to those of the structurally analogous oxarhenacycle **3** [1]. The signal of the *C*OEt carbon atom of **1** at δ 243.7 moves upfield to δ 179.6 and 184.6 in **5** and **3**, respectively. However, the signal of the undisturbed *C*CH_3 carbon atom experiences smaller shifts, from δ 246.4 for **1** to δ 212.9 for **5** and to δ 233.7 for **3**. Similar trends are noted among the ^1H NMR spectra of these compounds. Protons close to the site of insertion are much more affected compared to the remote protons. Thus, the chemical shift of the CCH_3 protons of **1** at δ 3.07 changes only to δ 2.82 in **5** and δ 2.91 in **3**, but to δ 2.38 in **4** and **2**. In contrast, the OCH_2 protons, at δ 4.70 in **1**, occur farther upfield in **5** and **3** (δ 4.13 and 4.39, respectively) than in **4** and **2** (δ 4.41 and 4.53, respectively). Like **4**, complex **5** exhibits a broad IR ν(NH) absorption (at 3390 cm^{-1}) and an NH ^1H NMR signal (at δ 5.9 (s br)).

Deprotonation of the azarhenacyclic complex 4

The resonance representations **I** and **II** (X = NH) that describe the structure of **4** (and **5**) are analogous to those that characterize organic pyrroles. Thus, complex **4** may be considered to be a rhenapyrrole. The parent pyrrole, C_4H_5N, is a weak acid, its pK_a being 17.5 [21]. It was thought that the presence of electron-withdrawing substituents on the rhenapyrrole ring of **4** (CO_2CH_3 and COs) might enhance the acidity of the NH proton. Raubenheimer *et al.* [5] showed that the imidate complex $(CO)_5WNH{=}C(OCH_3)Ph$ can be deprotonated by NaH, LiBu, NaOEt and NaSEt.

Complex **4** does not exchange the NH hydrogen with deuterium when allowed to react with an excess of D_2O in THF at room temperature for 2 days. However, deuterium exchange is observed when a solution of **4** in THF is treated with LDA at low temperature and the reaction is quenched by addition of 20% DCl in D_2O (eqn. (8)). The ^1H NMR spectrum of the product shows disappearance of both the broad NH signal and the small coupling associated with the CCH_3 signal. The presence of a singlet resonance at δ 6.98 in the ^2H NMR spectrum provides strong evidence for the replacement of hydrogen with deuterium on the nitrogen.



4

(8)

Supplementary material

Hydrogen atom positional parameters, anisotropic thermal parameters, least-squares planes, observed and calculated structure factors, and complete listings of bond distances and angles are available on request from the authors.

Acknowledgements

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