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Synthesis and molecular structure of *cisoid* and *transoid* isomers of $[Re_2(CO)_6(1,1'\text{-bis(indenylidene)})]$ derived from the reaction of $[Re_2(CO)_8(MeCN)_2]$ and diazoindene

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Abstract

The compound $[Re_2(CO)_8(MeCN)_2]$ reacts with diazoindene ($C_9H_6N_2$) while refluxing in THF to afford three dirhenium products in which $C_9H_6N_2$ is cleaved with loss of N_2 and with incorporation of the residual indenylidene group into the products. Two indenylidene groups are coupled in two diastereomers of $[Re_2(CO)_6(\mu,\eta^5{:}\eta^5\text{-}1,1'\text{-}C_{18}H_{12})]$ where $C_{18}H_{12}$ = bis(indenylidene). X-ray structures show that these isomers are related as *RR*/*SS* and *RS* isomers. These have the two $Re(CO)_3$ groups coordinated *transoid* and *cisoid*, respectively to a *trans* bis(indenylidene) bridge. The third product is the μ-indenylidene complex $[Re_2(CO)_8(\mu,\eta^1{:}\eta^5\text{-}C_9H_6)]$, which was also structurally characterised by X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Diazoindene; Bis(indenylidene) isomers; μ-Indenylidene; Rhenium carbonyls

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1. Introduction

Diazoalkenes have been used to react with metal–metal bonded compounds to form transition metal complexes containing μ-CH_2, or more generally μ-CR_2. By use of diazocyclopentadiene ($C_5H_4N_2$), complexes containing σ- or π-bonded $C_5H_4N_2$ have been formed [1] and in some cases monohalocyclopentadienyl complexes have been derived from halo-complexes [2]. Recently, substituted $RCpRe(CO)_3$ complexes (R = halo-, carbonyl-, oxy- and hidroxy-) have been obtained using $C_5H_4N_2$ as the Cp precursor [3]. However, more commonly cleavage of N_2 from C_5H_4 of diazocyclopentadiene occurs to give organo-bridged di- or polynuclear products. For example, we reported recently the insertion of C_5H_4 from diazocyclopentadiene or C_9H_6 from diazoindene into the metal–metal bonds of $[Ru_3(CO)_{12}]$ to produce the complexes $[Ru_3(CO)_{10}(\mu,\eta^1{:}\eta^5\text{-}C_5H_4)]$ with the cyclopentadienylidene ligand bridging a pair of ruthenium atoms, and $[Ru_3(CO)_6(\mu,\eta^1{:}\eta^5\text{-}L)_3]$ containing the ligand L (C_5H_4 or C_9H_6) bridging each pair of ruthenium atoms [4,5]. These results confirm that these diazo-compounds are excellent sources of μ,$\eta^1{:}\eta^5$-cyclopentadienylidene or μ,$\eta^1{:}\eta^5$-indenylidene. Relevant to this present communication, the indenylidene complex $[Ru_3(CO)_6(\mu,\eta^1{:}\eta^5\text{-}L)_3]$ is formed as isomers differing in the relative orientations of the benzo groups with respect to the Ru_3 triangle (up, up, up or up, up, down) whereas only one C_5H_4 isomer is possible.

2. Results and discussion

The incorporation of C_5H_4 or C_9H_6 is facilitated by having labile ligands present in the starting metal com-

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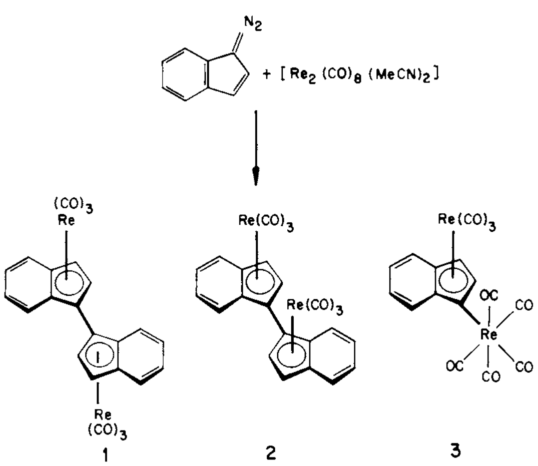

Scheme 1.

plex. Thus $C_5H_4N_2$ reacts readily with $[Re_2(CO)_8(MeCN)_2]$ to lead to various products containing the C_5 rings and one product which still contains nitrogen, the dinuclear derivative $[Re_2(CO)_8(C_{10}H_8N_2)]$ [6]. We now report the corresponding reaction of diazoindene with $[Re_2(CO)_8(MeCN)_2]$ to give new dirhenium products containing μ-C_9H_6 or the coupled ligand μ-$C_{18}H_{12}$. No products containing nitrogen were obtained in this case. Thus reaction of $[Re_2(CO)_8(MeCN)_2]$ with diazoindene in a molar ratio 2.7 mol per mol Re_2 (other ratios gave the same products but lower yields) in refluxing THF for 2 h gave three compounds which were separated by TLC on silica: $[Re_2(CO)_6(\mu,\eta^5{:}\eta^5\text{-}1,1'\text{-}C_{18}H_{12})]$ where $C_{18}H_{12}$ = bis(indenylidene), as isomers **1** and **2**, and the μ-indenylidene complex $[Re_2(CO)_8(\mu,\eta^1{:}\eta^5\text{-}C_9H_6)]$ **3**, each of which was obtained as orange or yellow crystals (Scheme 1). Notably compounds **1** and **2** were not formed in the reaction of bis(indenylidene) with $[Re_2(CO)_8(MeCN)_2]$ under the same conditions and therefore the C–C coupling reaction must have occurred between rhenium coordinated C_9H_6 fragments rather than by preliminary formation of bis(indenylidene).

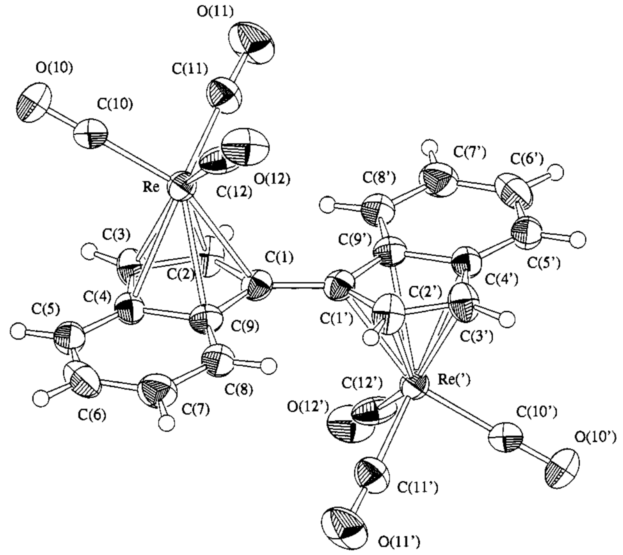

Fig. 1. ORTEP diagram (35% displacement ellipsoids) for the *meso* (RS) isomer of $[Re_2(CO)_6(\mu,\eta^5{:}\eta^5\text{-}1,1'\text{-}C_{18}H_{12})]$.

Compounds **1** and **2** give indistinguishable IR ν(CO) spectra, consistent with each containing two equivalent $Re(CO)_3$ groups in identical chemical environments. The ^{1}H-NMR spectra are also similar but differ in detail. The X-ray structure of each (Figs. 1 and 2) was determined to establish the origin of the isomerism. Crystal data are given in Table 1 and selected bond lengths and angles are given in Table 2. Complexation to a five membered ring of bis(indenylidene) to $Re(CO)_3$ generates a chiral centre and therefore the complex $[Re_2(CO)_6(\mu,\eta^5{:}\eta^5\text{-}1,1'\text{-}C_{18}H_{12})]$ with two such centres exists as a *meso* form with C_i symmetry (*RS*) (isomer **1**) and a racemic form with C_2 symmetry (*RR*/*SS*) (isomer **2**). In their crystal structures the bridging bis(indenylidene) ligands in both **1** and **2** are *transoid* about the central C–C bond since the *cisoid* form would contain an unfavourable C(8)H···C(8′)H contact. There may be a significant activation barrier for rotation about this bond as a result of residual pπ–pπ bonding [C(1)–C(1′) lengths: 1.45(1) Å in **1** and 1.40(1) Å in **2**], favouring an approximately planar ligand arrangement. Compound **1** is centrosymmetric and therefore the bis(indenylidene) is planar whereas there is a marked twist about this central bond in the isomer **2** with a dihedral angle Re–C(1)–C(1′)–Re′ = 47.0(2)°, which would reduce the pπ–pπ bonding in the central C(1)–C(1′) bond. As a result of the favoured *trans* bis(indenylidene) arrangement in each isomer, the $Re(CO)_3$ groups are on opposite sides of the ligand in **1** and on the same side in **2**. The twist in **2** with $Re(CO)_3$ groups on the same side is required to prevent these groups coming too close to each other. There is there-

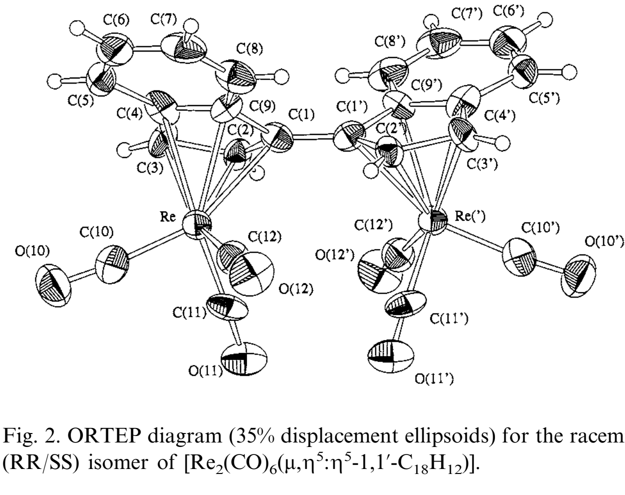

Fig. 2. ORTEP diagram (35% displacement ellipsoids) for the racemic (RR/SS) isomer of $[Re_2(CO)_6(\mu,\eta^5{:}\eta^5\text{-}1,1'\text{-}C_{18}H_{12})]$.

Table 1
Crystal data collection and refinement for compounds **1**, **2** and **3**[a]

Compound	**1**	**2**	**3**
Formula	$C_{24}H_{12}O_6Re_2$	$C_{24}H_{12}O_6Re_2$	$C_{17}H_6O_8Re_2$
M	768.74	768.74	710.63
Colour	Orange	Yellow	Orange
Specimen size (mm^3)	$0.08 \times 0.12 \times 0.40$	$0.08 \times 0.10 \times 0.36$	$0.04 \times 0.06 \times 0.38$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$
a (Å)	8.434(5)	13.735(7)	9.788(6)
b (Å)	8.490(4)	7.467(10)	26.590(4)
c (Å)	7.676(5)	21.090(4)	13.707(6)
α (°)	100.11(7)	90	90
β (°)	94.39(6)	90.28(3)	92.35(4)
γ (°)	76.82(4)	90	90
V (Å^3)	526.5(5)	2163(3)	3564(3)
Z	1	4	8
$D_{calc.}$ (g cm^{-3})	2.425	2.361	2.649
μ(Mo–K$_\alpha$) (cm^{-1})	11.53	11.22	13.62
F(000)	354	1416	2576
h, k, l range	0, −9, −9–10, 10, 9	0, 0, −25–16, 8, 25	−1, −31, 0–11, 31, 16
Total data	1990	2073	7555
Unique data	1851	1910	3791
Abs. cor.	DIFABS	DIFABS	ψ Scan
g (extinction parameter)[b]	0.0005(8)	0.00013(1)	
Reflections used	1851	1664	3791
Parameters	147	146	489
R[c]	0.0327	0.0570	0.0256
R_w[d]	0.0825	0.1160	0.0427
S (GOF)[e]	1.023	1.064	1.017
Maximum shift/Estimated S.D.	0.001	0.016	0.013
Maximum peak in final diff. Fourier (e Å^{-3})	1.561	2.362	0.587

[a] For each crystal: number of orientation reflections = 25 within the range $3 \leq 2\theta \leq 50$, scan mode $\omega - 2\theta$, rejection criterion, $I_o \leq 2\sigma(I_o)$.

[b] $|F_c^*| = k|F_c| \, [gI_o + (1 + g^2 I_o^2)^{1/2}]^{-1/2}$.

[c] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[d] $R_w = [\Sigma w(|F_o| - |F_c|)^2 = \Sigma w|F_o|^2]^{1/2}$.

[e] $S = \Sigma w(|F_o| - |F_c|)^2/(n - m)$, n = observations, m = parameters.

fore no driving force for such a twist in **1** and therefore the molecule is centrosymmetric. Isomerism of **1** to **2** would require the movement of one Re(CO)$_3$ group to the opposite ligand face and cannot occur by any low energy process and we found no evidence for their interconversion.

The molecular structure of chiral compound **3** shown in Fig. 3 is as expected for a bridging indenylidene dirhenium complex and relates to the structure of the corresponding cyclopentadienylidene complex, the structure of which is also known [6]. In each of the η^5 indenyl-type systems **1** to **3** there is the expected small slippage leading to shorter Re–C bonds to C(2) and C(3) (Table 3).

3. Experimental

Compounds [Re$_2$(CO)$_8$(MeCN)$_2$] [7] and diazoindene [8] were prepared as described in the literature.

3.1. Synthesis of *1*, *2* and *3*

Freshly distilled diazoindene (0.050 cm^3, 0.40 mmol) was added to a solution of [Re$_2$(CO)$_8$(MeCN)$_2$] (0.100 g, 0.15 mmol) in pure dried THF (50 cm^3) under nitrogen and the solution was refluxed while the course of the reaction was monitored by IR spectroscopy to establish when the reaction was complete (2 h). Low pressure removal of volatiles and TLC of the residue yielded **1** as orange crystals (0.018 g, 16%) from n-hexane/dichloromethane. Found: C, 37.45; H, 1.46. Anal. Calc. for $C_{24}H_{12}O_6Re_2$: C, 37.50; H, 1.56. Compound **2** as yellow crystals (0.015 g, 13%) from cyclohexane. Found: C, 37.41; H, 1.42. Anal. Calc. for $C_{24}H_{12}O_6Re_2$: C, 37.50; H, 1.56 and **3** as orange crystals (0.020 g, 19%) from n-hexane. Found: C, 28.68; H, 0.72. Anal. Calc. for $C_{17}H_6O_8Re_2$: C, 28.74; H, 0.84. Crystals suitable for single-crystal structure determination were obtained from these solvents.

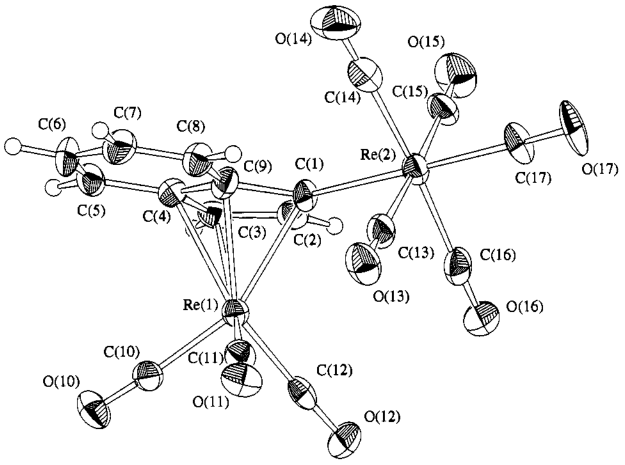

Fig. 3. ORTEP diagram (35% displacement ellipsoids) for molecule A of the μ-indenylidene complex $[Re_2(CO)_8(\mu,\eta^1{:}\eta^5\text{-}C_9H_6)]$. Molecule B is very closely similar.

*3.2. Selected spectroscopic data for **1**, **2** and **3***

IR spectra were measured for cyclohexane solutions and NMR spectra were recorded in CD_3COCD_3 at 300 MHz and 296 K. Compound **1**: ν(CO)/cm^{-1}: 2036 m, 2025 s, 1939 vs. ^{1}H-NMR: δ 7.90 (ddd, H^3), 7.76 (ddd, H^6), 7.36 (ddd, H^4), 7.26 (ddd, H^5), 6.50 (d, H^1), 6.22 (dd, H^2), $J_{12} = 3.0$, $J_{23} = 0.9$, $J_{34} = 8.8$, $J_{35} = 1.9$, $J_{45} = 6.6$, $J_{46} = 1.1$, $J_{56} = 6.6$ Hz. Compound **2**: ν(CO)/cm^{-1}: 2036 m, 2025 s, 1939 vs. ^{1}H-NMR: δ 7.74 (m, H^6), 7.63 (m, H^3), 7.24 (m, H^4, H^5), 6.40 (d, H^1), 6.26 (dd, H^2), $J_{12} = 3.0$, $J_{23} = 0.9$ Hz (other J unresolved). Compound **3**: ν(CO)/cm^{-1}: 2046 w, 2028 vs, 1996 m, 1990 s, 1963 w, 1940 m, 1932 s, 1920 m. ^{1}H-NMR: δ 7.59 (m, H^3, H^6), 7.06 (m, H^4, H^5), 6.04 (dd, H^2), 5.85 (d, H^1), $J_{12} = 2.5$, $J_{23} = 1.0$ Hz (other J unresolved).

*3.3. Crystal structure determinations for compounds **1**, **2** and **3***

All measurements were carried out at 293(2) K on a Rigaku AFC7S diffractometer, using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). Crystal data, intensity data collection parameters and final refinement results are summarized in Table 1. Intensity data were scaled on the basis on intensities of check reflections monitored every 150 measurements and were corrected for Lorentz and polarization effects. In the latter stages of refinement empirical absorption and isotropic extinction corrections were applied. Space group determinations were assisted by the systematic absences. The structures were solved by direct methods [9], expanded using Fourier techniques [10] and refined on F by full-matrix least-squares with weights $w = \sigma(F)^{-2}$. The hydrogen atoms were placed in calculated positions (C–H = 0.96 Å) and assigned fixed coordinates but their isotropic displacement parameters were refined. All non-hydrogen atoms were refined anisotropically. The largest residual electron density peaks were in the neighborhood of the heavy atoms. For compounds **1** and **2**, half of each molecule is symmetry related to the other half by a centre of symmetry for **1** and a two-fold rotation axis for **2**. For **3** there are two very similar but independent molecules in the unit cell.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

	Compound **1**	Compound **2**
Re–C(1)	2.332(8)	2.35(2)
Re–C(2)	2.282(9)	2.29 (2)
Re–C(3)	2.28(1)	2.28(2)
Re–C(4)	2.356(9)	2.34(2)
Re–C(9)	2.380(8)	2.38(2)
Mean value Re–C(n)		
($n = 2, 3$)	2.280	2.29
($n = 1, 4, 9$)	2.356	2.36
Re(1)–C(1)–C(1′)	125.3	130.2
C(9)–C(1)–C(1′)	129.8	125.2
C(2)–C(1)–C(1′)	125.2	129.5

Table 3
Selected bond lengths (Å) and angles (°) for compound **3**[a]

	Molecule A	Molecule B
Re(1)–C(1)	2.35(1)	2.35(1)
Re(1)–C(2)	2.26(1)	2.28(1)
Re(1)–C(3)	2.267(8)	2.272(9)
Re(1)–C(4)	2.345(8)	2.354(8)
Re(1)–C(9)	2.335(9)	2.349(9)
Re(2)–C(1)	2.20(1)	2.19(1)
Mean value Re–C(n)		
($n = 2, 3$)	2.261	2.276
($n = 1, 4, 9$)	2.343	2.351
Re(1)–C(1)–Re(2)	131.6(5)	132.4(5)
Re(2)–C(1)–C(2)	128.4(7)	126.6(7)
Re(2)–C(1)–C(9)	128.9(7)	130.2(8)

[a] Data are given for molecule A with the corresponding data for molecule B.

The MSC/AFC diffractometer control software [11] was used for data collection and cell refinement. All other calculations and drawings were made using the TEXSCAN software package [12]. Neutral-atom scattering factors were taken from reference [13], anomalous scattering corrections from reference [14] and mass absorption coefficients from reference [15].

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 109836 for compound **1**, 109837 for compound **2** and 109838 for compound **3**.

Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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