Synthesis of [$Re_2(CO)_8\{\mu\text{-}N_2(C_5H_4)_2\}$], Derived from the Reaction of [$Re_2(CO)_8(MeCN)_2$] and Diazocyclopentadiene

Ysaura De Sanctis,* Alejandro J. Arce, Rubén Machado,
Mario V. Capparelli, and Reinaldo Atencio

*Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC),
Apartado 21827, Caracas 1020-A, Venezuela*

Antony J. Deeming

*Department of Chemistry, University College London, 20 Gordon Street,
London WC1H 0AJ, U.K.*

Jorge Manzur

*Departamento de Química, Universidad de Chile, Av. Tupper 2069, Casilla 2777,
Santiago, Chile*

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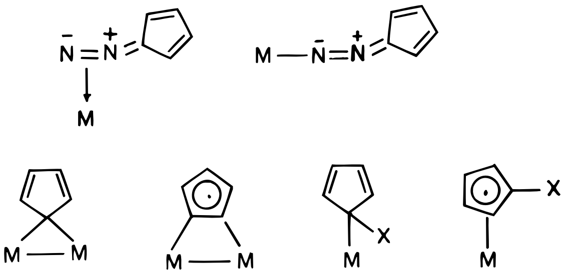
*Summary: The reaction of [$Re_2(CO)_8(MeCN)_2$] with diazocyclopentadiene in refluxing tetrahydrofuran in a 1:1 molar ratio gave [$Re(CO)_3(C_5H_5)$] (**1**), the cyclopentadienylidene complex [$Re_2(CO)_8(\mu,\eta^1:\eta^5\text{-}C_5H_4)$] (**2**), and the fulvalene complex [$Re_2(CO)_6(\mu,\eta^5:\eta^5\text{-}C_{10}H_8)$] (**3**) in moderate overall yield. A similar reaction in a 1:2 molar ratio gave almost exclusively the new compound [$Re_2(CO)_8\{\mu\text{-}N_2(C_5H_4)_2\}$] (**4**) containing a novel diazo-bridging ligand.*

Cyclopentadienyl metal complexes are of major importance in organometallic chemistry, in organic synthesis, and in catalysis. New variations of the ligand are continually being developed.[1,2] For example, the synthetic use of diazocyclopentadiene ($C_5H_4N_2$) has made monohalocyclopentadienyl complexes readily accessible.[3] However, the interaction of diazocyclopentadiene with transition metal compounds is interesting in its own right and is known to generate at least six types of ligand systems, as shown in Scheme 1. Some systems are based on σ- or π-bonded $C_5H_4N_2$ and on μ-C_5H_4, and other systems are derived from the nucleophilic addition of X^- to C_5H_4 to give the monosubstituted ligand C_5H_4X.[4]

Scheme 1



Cleavage of the diazo-compound $C_5H_4N_2$ with loss of N_2 is almost always observed in its interaction with dinuclear metal complexes of group 8. For example, Herrmann has shown that diazocyclopentadiene reacts with the metal−metal triple bond of [$Mo_2(CO)_4Cp_2$] to afford the cyclopentadienylidene derivative [$Mo_2(CO)_3(\eta^5\text{-}Cp)_2(\mu,\eta^1:\eta^5\text{-}C_5H_4)$] ($N_2$ and CO elimination) containing a single Mo−Mo bond.[5] In this complex, the organic ligand is σ-bonded to a [$(\eta^5\text{-}Cp)Mo(CO)_2$] fragment and η^5-bonded to a [$(\eta^5\text{-}Cp)Mo(CO)$] unit. We recently reported the insertion of C_5H_4 units from $C_5H_4N_2$ into metal−metal bonds of [$Ru_3(CO)_{12}$] to afford complexes of the type [$Ru_3(CO)_{10}(\mu,\eta^1:\eta^5\text{-}C_5H_4)$] and [$Ru_3(CO)_6(\mu,\eta^1:\eta^5\text{-}C_5H_4)_3$], thus establishing that $C_5H_4N_2$ is an effective precursor for the insertion of C_5H_4 units into metal−metal bonds.[6]

Here, we report the insertion of one or two C_5H_4 units from $C_5H_4N_2$[7] into the dinuclear labile compound [$Re_2(CO)_8(MeCN)_2$][8] in refluxing THF to give complexes **1** (20%), **2** (13%), and **3** (11%), if the reaction is carried out in a 1:1 molar ratio (Scheme 2).[9]

Compounds **2** and **3** are derived from $C_5H_4N_2$ by loss of N_2, while the formation of compound **1** requires H-abstraction, presumably from solvent. Compounds **1**,[10] **2**,[11] and **3**[12] were shown spectroscopically to be the same as the published compounds. The X-ray structure of **1** is known,[10b] but since those of the dinuclear derivatives **2** and **3** have not been reported, we determined these in this work.[13] These structures (Figures 1 and 2) are as expected and do not justify further discussion.

However, if the reaction between $C_5H_4N_2$ and [$Re_2(CO)_8(MeCN)_2$] is conducted with a 2-fold excess of the ligand, an unprecedented diazodicyclopentadiene-bridged complex **4** is obtained almost exclusively (Scheme 2). Thus, reaction of [$Re_2(CO)_8(MeCN)_2$] with diazocyclo-

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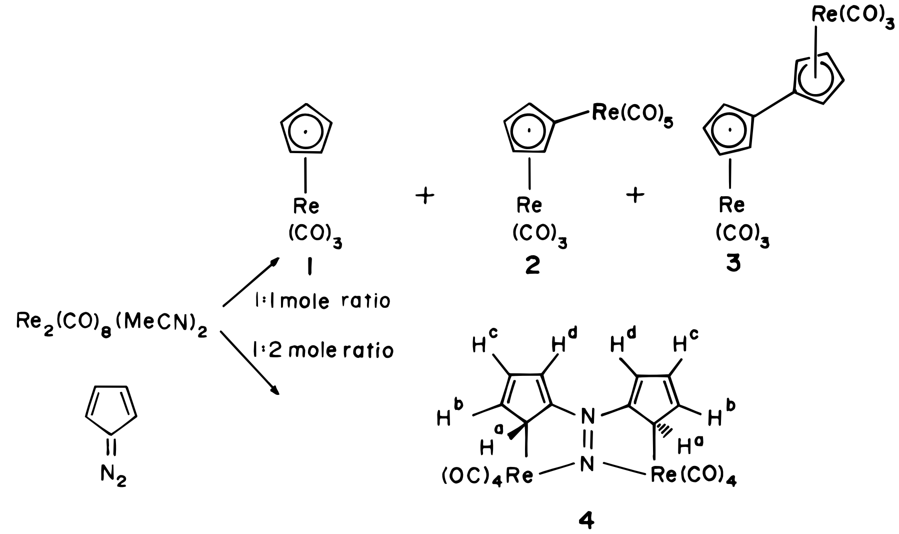
Scheme 2



pentadiene in a 1:2 molar ratio in refluxing THF for 20 min gave pure [$Re_2(CO)_8\{\mu$-$N_2(C_5H_4)_2\}$], **4**, isolated in 72% yield, and only trace amounts of compounds **1**, **2**, and **3** were obtained.[9] An X-ray analysis of **4** confirmed that it is a dinuclear derivative of C_2 symmetry.[13]

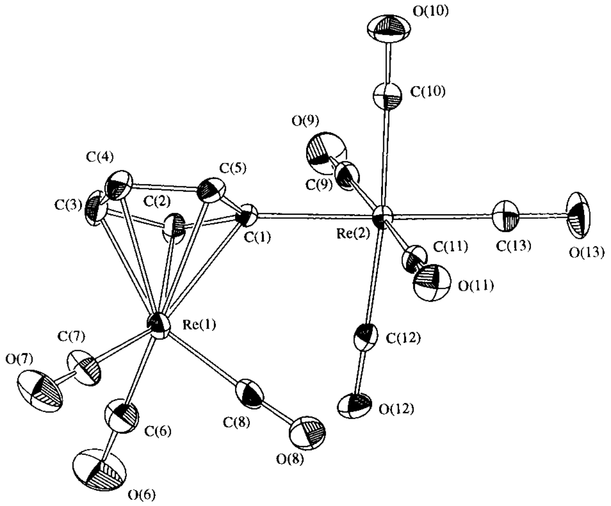


Figure 1. ORTEP plot of **2** (35% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Re(1)–C(1) = 2.348(6), Re(1)–C(2) = 2.283(8), Re(1)–C(3) = 2.291(9), Re(1)–C(4) = 2.292(9), Re(1)–C(5) = 2.298(7), Re(2)–C(1) = 2.206(6), Re(1)–C(1)–Re(2) = 130.2(3), Re(2)–C(1)–C(2) = 126.9(5), Re(2)–C(1)–C(5) = 127.5(5).

The new diazo-ligand bridges the rhenium atoms symmetrically as a 6-electron donating unit through a μ-N coordination and two Re–C σ bonds (Re(1)–C(1) = 2.311(6) Å and Re(2)–C(10) = 2.309(7) Å, Figure 3). The angle Re(1)–N(1)–Re(2) is 135.0(2)°, and the Re···Re contact (3.966(2) Å) precludes any direct metal–metal bonding. The distances Re(1)–N(1) = 2.144(5) Å and Re(2)–N(1) = 2.149(4) Å indicate a symmetrical bridge. Ligands of the type R_2NN may be described as hydrazine-1,1-diyl dianions or as neutral isodiazenes. In [$Mn_2(\eta^5$-$Cp)_2\{\mu$-$NN(SiMe_3)_2\}_2$],[14] the N–N distance is 1.439(10) Å and in [$Ti_2Cl_2(\eta^5$-$C_5H_5)_2(\mu$-$NNPh_2)_2$],[15] it is 1.390(4) Å for the μ,η^1 ligand (the other N_2Ph_2 ligand is

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[9] All of the reactions were performed under a nitrogen atmosphere. Solvents were purified by standard methods and distilled prior to use. [$Re_2(CO)_8(MeCN)_2$][8] and $C_5H_4N_2$[7] were prepared by published procedures. Other reagents were purchased from Aldrich and were used as supplied. IR spectra were recorded in cyclohexane, and ^1H NMR were obtained at 300 MHz. *Synthesis of **1**, **2**, and **3***. One hundred milligrams of [$Re_2(CO)_8(MeCN)_2$] (1.2 mmol) was dissolved in 50 mL of tetrahydrofuran under N_2. One hundred and six milligrams (1.2 mmol) of freshly distilled diazocyclopentadiene was added, and the solution was refluxed for 1 h, during which time the color changed from pale yellow to light orange. The volatile materials were removed under vacuum, and the residue was separated by TLC, using hexane as the eluant, to yield pure [$Re(CO)_3(C_5H_5)$] (**1**, 20 mg, 20%), [$Re_2(CO)_8(\mu,\eta^1{:}\eta^5$-$C_5H_4)$] (**2**, as colorless crystals from cyclohexane, 26 mg, 13%), and [$Re_2(CO)_6$-$(\mu,\eta^5{:}\eta^5$-$C_{10}H_8)$] (**3**, as colorless crystals from *n*-hexane, 20 mg, 11%). **1**: IR ν(CO) 2030 (s), 1939 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 296 K) δ 5.35 (s, 5H). Anal. Calcd (found) for $C_8H_5O_3Re$: C, 28.65 (27.50); H, 1.50 (1.38). **2**: IR ν(CO) 2029 (vs), 1999 (s), 1932 (s), 1920 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 296 K) δ 5.34 (m, 2H), 5.23 (m, 2H). Anal. Calcd (found) for $C_{13}H_4O_8Re_2$: C, 23.63 (22.68); H, 0.61 (0.56). **3**: IR ν(CO) 2027 (s), 1989 (m), 1943 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 296 K) δ 5.53 (m, 4H), 5.30 (m, 4H). Anal. Calcd (found) for $C_{16}H_8O_6Re_2$: C, 28.74 (27.30); H, 1.20 (1.10). *Synthesis of **4***. The reaction was carried out as above, but in a mol ratio of [$Re_2(CO)_8(MeCN)_2$]:$C_5H_4N_2$ = 1:2. One main product was isolated by TLC, [$Re_2(CO)_8\{\mu$-$N_2(C_5H_4)_2\}$] (**4**), as a red solid (80 mg, 72%); trace amounts of **1**, **2**, and **3** were also obtained. Crystals of **4** suitable for X-ray diffraction were obtained from slow evaporation of a *n*-hexane solution. **4**: IR ν(CO) 2100 (w), 2088 (w), 2006 (vs), 1993 (m), 1956 (sh), 1945 (s) cm^{-1}; ^1H NMR (CD_3COCD_3, 296 K) δ 7.28 (ddd, J = 1.2, 1.6, 4.4 Hz, H^b), 7.14 (dd, J = 1.2, 3.1 Hz, H^d), 6.70 (dd, J = 3.1, 4.4 Hz, H^c), 5.32 (d, J = 1.6 Hz, H^a). Anal. Calcd (found) for $C_{18}H_8N_2O_8Re_2$: C, 28.72 (27.37); H, 1.07 (0.97).

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(13) Crystal data. **2**: $C_{13}H_4O_8Re_2$, triclinic, space group $P\bar{1}$ (No. 2), a = 8.639(4) Å, b = 12.677(3) Å, c = 7.308(3) Å, α = 93.93(2)°, β = 98.30(3)°, γ = 82.49(3)°, V = 784.2(5) Å^3, Z = 2, 3609 unique reflections (R_{int} = 0.0341), agreement factors $R(F)$ = 0.0347 and $wR2(F^2)$ = 0.0902 for 2995 observed reflections [$I > 2.0\sigma(I)$]; SHELXL-93 program was used for refinement. **3**: $C_{16}H_8O_6Re_2$, monoclinic, space group $P2_1/a$ (No. 14), a = 7.238(2) Å, b = 10.929(3) Å, c = 10.526(4) Å, β = 104.28(4)°, V = 806.9(8) Å^3, Z = 2, 1962 unique reflections (R_{int} = 0.021). Full-matrix least-square refinement on F based on 1368 observed reflections [$I > 2.0\sigma(I)$], agreement factors $R(F)$ = 0.030 and $Rw(F)$ = 0.027; calculations were made using the *teXsan* package. **4**: $C_{18}H_8N_2O_8Re_2$, monoclinic, space group $P2_1/c$ (No. 14), a = 10.046(4) Å, b = 17.490(4) Å, c = 12.325(5) Å, β = 111.52(4)°, V = 2014(1) Å^3, Z = 4, agreement factors $R(F)$ = 0.0248 and $wR2(F^2)$ = 0.0640 for 3628 observed reflections [$I > 2.0\sigma(I)$]; SHELXL-93 program was used for refinement. Structures were determined at room temperature on a Rigaku AFC7S diffractometer using Mo Kα radiation (λ = 0.710 69 Å). See the Supporting Information for details on data collection and structure determination.

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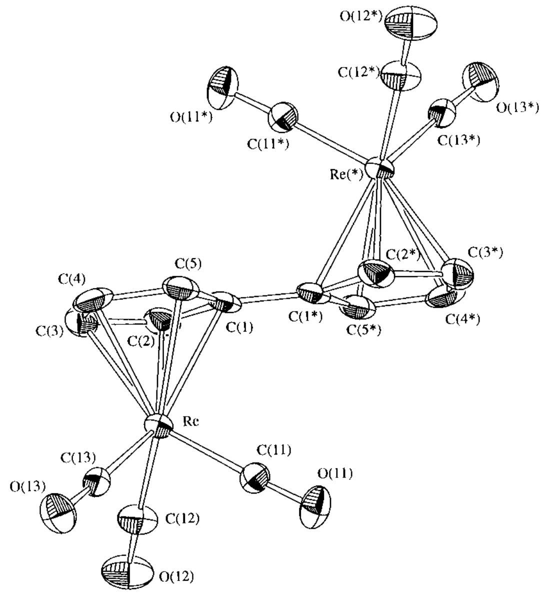


Figure 2. ORTEP plot of **3** (35% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Re(1)–C(1) = 2.324(8), Re(1)–C(2) = 2.295(8), Re(1)–C(3) = 2.290(10), Re(1)–C(4) = 2.293(9), Re(1)–C(5) = 2.304(9), C(1)–C(1*) = 1.45(2), Re–C(1)–C(1*) = 124.3(8). Atoms labeled with asterisks were generated by a symmetry center.

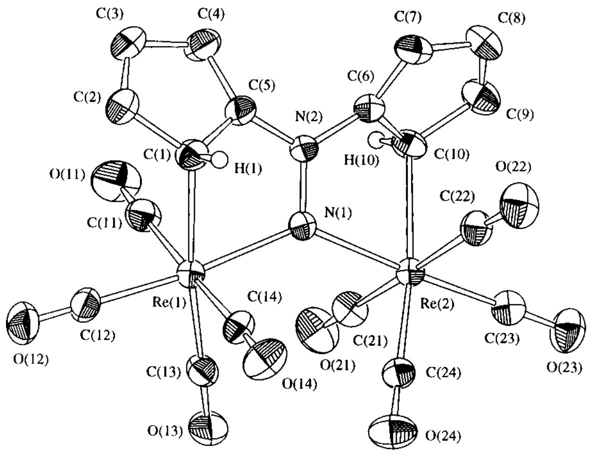
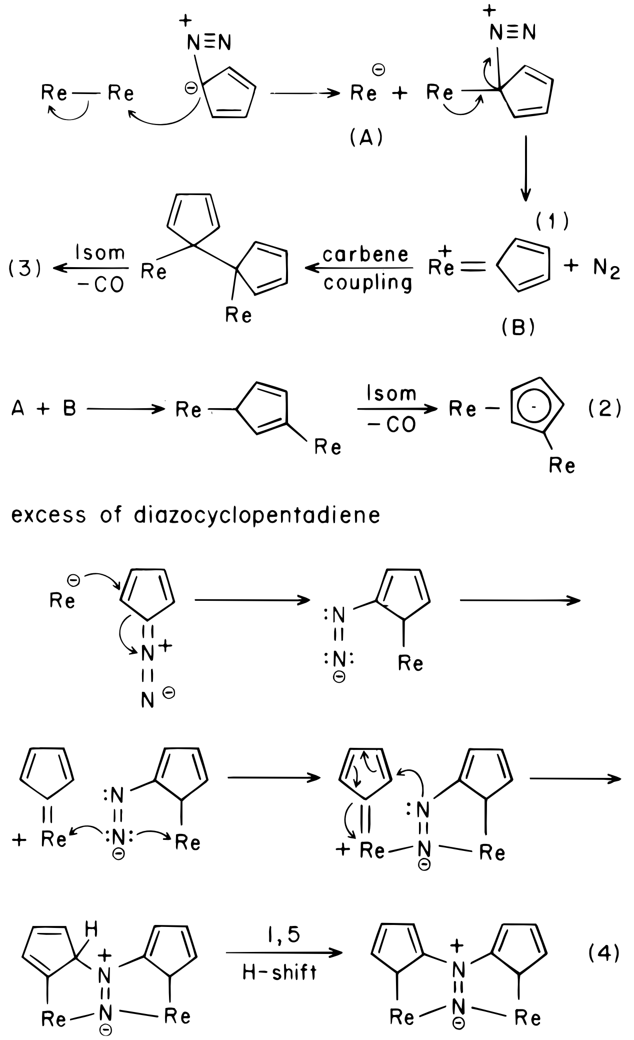


Figure 3. ORTEP plot of **4** (35% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Re(1)–N(1) = 2.144(5), Re(1)–C(1) = 2.311(6), Re(2)–N(1) = 2.149(4), Re(2)–C(10) = 2.309(7), N(1)–N(2) = 1.308(7), N(2)–C(5) = 1.402(7), N(2)–C(6) = 1.414(8), C(1)–C(2) = 1.438(9), C(1)–C(5) = 1.462(9), C(2)–C(3) = 1.360(11), C(3)–C(4) = 1.425(9), C(4)–C(5) = 1.364(10), C(6)–C(7) = 1.360(11), C(6)–C(10) = 1.461(7), C(7)–C(8) = 1.421(10), C(8)–C(9) = 1.343(12), C(9)–C(10) = 1.444(11), N(1)–Re(1)–C(1) = 77.4(2), N(1)–Re(2)–C(10) = 77.0(2), Re(1)–N(1)–Re(2) = 135.0(2), Re(1)–N(1)–N(2) = 112.1(4), Re(2)–N(1)–N(2) = 112.8(4), N(1)–N(2)–C(5) = 118.7(5), N(1)–N(2)–C(6) = 117.1(5), C(5)–N(2)–C(6) = 124.1(5).

bonded through both N atoms). Both distances are considered to be close to single N–N bond lengths, whereas the much shorter N(1)–N(2) distance in **4** (1.308(7) Å) is much closer to that expected for N=N. We prefer, therefore, to describe the ligand in **4** as an isodiazene.

Formation of five-membered rings by 1,4-N,C coordination of the diazocyclopentadiene to a metal is unprecedented, to the best of our knowledge. Metallocyclobutane complexes with 1,3-N,C coordination of the diazoalkane ([1 + 3] cycloadducts) have been postulated as intermediates in the catalytic decomposition of diazoalkanes, leading to coordinated carbenes or, more commonly, products of their reactions.[16] Cycloadducts of this kind are usually sensitive to decomposition by elimination of N_2. We have not established a mechanism for the formation of **4**, but a possible description is shown in Scheme 3. It involves heterolysis of the Re–Re bond to give the $Re(CO)_4^-$ species **A**, and the metallocarbene $(CO)_4ReC_5H_4^+$, **B**, which account for the formation of **1**, **2**, and **3**; with excess diazocyclopentadiene, **4** is obtained at the expense of **1**, **2**, and **3**. For compound **4**, Re forms a σ-bond at the 2-position of the C_5 ring of $C_5H_4N_2$ instead of at the 1-position, as in the formation of **2** and **3**. This implies a quite different process from that which gives **1**, **2**, and **3**.

Scheme 3



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Supporting Information Available: Experimental details for the X-ray structure determinations, tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, and anisotropic displacement parameters for compounds **2**, **3**, and **4** (52 pages). Ordering information is given on any current masthead page.

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