mechanism and general scope of application of this reaction are now under investigation.

Experimental Section

1 and **2**: A solution of $[Cp^*_2Ru_2S_4]$ (161 mg, 0.268 mmol) in toluene (15 mL) was added to a solution of $[W(CO)_3(MeCN)_3]$ in acetonitrile, which was prepared by refluxing a solution of $[W(CO)_6]$ (189 mg, 0.536 mmol) in acetonitrile (5 mL). The mixture was heated with stirring at 50 °C for 40 min. The volatile components were removed under reduced pressure, and the residue was extracted with toluene/hexane (1/1, 10 mL). Compounds **1** and **2** were obtained from the extracted solution and the insoluble material as follows: the extracted solution was subjected to flash column chromatography (silica gel, eluent toluene/hexane (1/1)). A red-brown fraction was concentrated to give **1** in 58 % yield. An analytically pure sample was obtained by recrystallization from dichloromethane/hexane. The insoluble dark brown residue was dissolved in dichloromethane and subjected to flash column chromatography (silica gel, eluent dichloromethane). The red-brown fraction was collected, and the solution was concentrated to give red-brown **2** in 11 % yield. Analytically pure **2** was obtained by recrystallization from toluene/hexane.

1: Elemental analysis calcd for $C_{26}H_{30}O_6Ru_2S_4W_2$: C 27.48, H 2.66; found C 27.83, H 2.74; MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): m/z: 1138 $[M^+]$; IR (KBr): $\tilde{\nu}_{max}\,[cm^{-1}] = 2031, 1975, 1959, 1921, 1848\ \nu_{(CO)}$; ^1H NMR ($[D_6]$benzene): $\delta = 1.68$ (s, 30 H, Cp*); ^{13}C NMR ($[D_6]$benzene): $\delta = 207.8$, 204.3, 200.5 (CO), 100.5 (C_5Me_5), 10.2 (C_5Me_5); UV/Vis (toluene): λ_{max} [nm] ($\varepsilon\,[cm^{-1}M^{-1}]$) = 314 ($1.7\times10^4$), 349 ($1.5\times10^4$), 408 ($1.2\times10^4$), 480 (sh), 535 (sh).

2: Elemental analysis calcd for $C_{26}H_{30}O_6Ru_2S_4W_2$: C 27.48, H 2.66; found C 27.71, H 2.95; MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix): m/z: 1138 $[M^+]$; IR (KBr): $\tilde{\nu}_{max}\,[cm^{-1}] = 2019, 1975, 1905(sh), 1882\ \nu_{(CO)}$; ^1H NMR ($[D_6]$benzene): $\delta = 1.59$ (s, 30 H, Cp*); ^{13}C NMR ($[D_2]$dichloromethane): $\delta = 209.7$, 208.1, 205.3, 196.2 (CO), 100.4 (C_5Me_5), 10.3 (C_5Me_5); UV/Vis (toluene): λ_{max} [nm] ($\varepsilon\,[cm^{-1}M^{-1}]$) = 325 ($2.4\times10^4$), 429 ($1.1\times10^4$), 510 ($8.2\times10^3$), 682 ($2.3\times10^3$).

Received: February 13, 1998 [Z 11478 IE]
German version: *Angew. Chem.* **1998**, *110*, 2232 – 2234

Keywords: clusters · isomerizations · ruthenium · sulfur · tungsten

---

[1] J. Wachter, *Angew. Chem.* **1989**, *101*, 1645 – 1658; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1613 – 1626, and references therein.

[2] T. Mitsui, S. Inomata, H. Ogino, *Inorg. Chem.* **1994**, *33*, 4934 – 4936.

[3] a) E. J. Houser, H. Krautscheid, T. B. Rauchfuss, S. R. Wilson, *J. Chem. Soc. Chem. Commun.* **1994**, 1283 – 1284; b) Q. Feng, T. B. Rauchfuss, S. R. Wilson, *J. Am. Chem. Soc.* **1995**, 117, 4702 – 4703; c) A. Venturelli, T. B. Rauchfuss, A. K. Verma, *Inorg. Chem.* **1997**, *36*, 1360 – 1365.

[4] T. B. Rauchfuss, D. P. S. Rodgers, S. R. Wilson, *J. Am. Chem. Soc.* **1986**, *108*, 3114 – 3115.

[5] D. P. Tate, W. R. Knipple, J. M. Augl, *Inorg. Chem.* **1962**, *1*, 433 – 434.

[6] Only one example of structurally characterized geometric isomers is known for sulfur clusters: a) P. Braunstein, J. M. Jud, A. Tiripicchio, M. Tiripicchio-Camellini, E. Sappa, *Angew. Chem.* **1982**, *94*, 318 – 319; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 307 – 308; b) P. D. Williams, M. D. Curtis, D. N. Duffy, W. M. Butler, *Organometallics* **1983**, *2*, 165 – 167.

[7] Crystal data for **1**: $C_{26}H_{30}O_6Ru_2S_4W_2$, $M_r = 1136.60$, crystal dimensions $0.50 \times 0.40 \times 0.25$ mm^3, $a = 22.41(1)$, $b = 13.432(6)$, $c = 11.148(3)$ Å, $\beta = 90.07(3)^\circ$, $V = 3355(2)$ Å^3, $T = 293$ K, monoclinic, space group $P2_1/n$ (no. 14), $Z = 4$, $\rho_{calcd} = 2.249\ g\,cm^{-3}$, $\rho_{found} = 2.23\ g\,cm^{-3}$, $F(000) = 2136$, $\mu = 80.08\ cm^{-1}$, Rigaku AFC6S diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), graphite monochromator, scan mode $\omega - 2\theta$, $2\theta_{max} = 55.0^\circ$, 8247 measured reflections, Lorentz-polarization and absorption correction (transmission factors: 0.7316 – 1.0000), 4762 observed reflections with ($I > 3\sigma(I)$), Patterson methods (DIRDIF92 PATTY), full-matrix least-squares refinement, 361 parameters, H atoms not located, $R = 0.045$ and $R_w = 0.065$ ($w = 1/(\sigma^2 F_o)$), max. residual electron density 1.09 e Å^{-3}. Crystal data for $\mathbf{2}\cdot 2\,CH_2Cl_2$: $C_{28}H_{34}Cl_4O_6Ru_2S_4W_2$, $M_r = 1306.47$, crystal dimensions $0.30 \times 0.20 \times 0.15$ mm^3, $a = 15.642(8)$, $b = 11.132(6)$, $c = 23.463(4)$ Å, $\beta = 96.64(2)^\circ$, $V = 4058(2)$ Å^3, $T = 293$ K, monoclinic, space group $P2_1/c$ (no. 14), $Z = 4$, $\rho_{calcd} = 2.138\ g\,cm^{-3}$, $\rho_{found} = 2.1\ g\,cm^{-3}$, $F(000) = 2472$, $\mu = 68.92\ cm^{-1}$, Rigaku AFC6S diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) graphite monochromator, scan mode $\omega - 2\theta$, $2\theta_{max} = 55.0^\circ$, 10 167 measured reflections, Lorentz-polarization, decay (27.4 %) and absorption correction (transmission factors: 0.7988 – 1.0000), 3634 observed reflections with ($I > 3\sigma(I)$), Patterson methods (DIRDIF92 PATTY), full-matrix least-squares refinement, 415 parameters, H atoms not located, $R = 0.056$ and $R_w = 0.075$ ($w = 1/(\sigma^2 F_o)$), max. residual electron density 2.12 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101 083. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] a) K. E. Howard, T. B. Rauchfuss, S. R. Wilson, *Inorg. Chem.* **1988**, *27*, 3561 – 3567; b) P. A. Shapley, Z. Gebeyehu, N. Zhang, S. R. Wilson, *ibid.* **1993**, *32*, 5646 – 5651; c) S. Ogo, T. Suzuki, K. Isobe, *ibid.* **1995**, *34*, 1304 – 1305; d) B. Zhuang, P. Yu, L. Huang, L. He, J. Lu, *Polyhedron* **1994** *13*, 125 – 131; e) W. J. Evans, M. A. Ansari, J. W. Ziller, S. I. Khan, *Organometallics* **1995**, *14*, 3 – 4; f) J. Ruiz, V. Rodríguez, G. López, P. A. Chaloner, P. B. Hitchcock, *J. Organomet. Chem.* **1995**, *493*, 77 – 82; g) Y. Mizobe, M. Hosomizu, Y. Kubota, M. Hidai, *J. Organomet. Chem.* **1996**, *507*, 179 – 185.

$[Re_5(\mu\text{-}H)_4(CO)_{20}]^-$ and $[Re_5(\mu\text{-}H)_5(CO)_{20}]$, Two Isolobal Analogues of Cyclopentane

Mirka Bergamo, Tiziana Beringhelli, Giuseppe D'Alfonso,* Pierluigi Mercandelli, Massimo Moret,* and Angelo Sironi

The $ReH(CO)_4$ fragment, isoelectronic with d^8 $M(CO)_4$, can be considered isolobal with (singlet) methylene,[1] as far as the formation of metal – metal interactions is concerned, since its frontier orbitals allow the interaction with two metal centers. The known $[ReH(CO)_4]_n$ oligomers ($n = 2-4$)[2] are therefore isolobal analogues of the corresponding $(CH_2)_n$ species: $[Re_2(\mu\text{-}H)_2(CO)_8]$ is an ethylene-like molecule,[2b] and the triangular and square-planar clusters $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ and $[Re_4(\mu\text{-}H)_4(CO)_{16}]$ "correspond" to cyclopropane and cyclobutane, respectively. Interestingly, until now no organometallic analogue of the most stable $(CH_2)_n$ oligomers (i.e., those with $n = 5$ or 6) was known. The pentanuclear cyclic clusters $[Re_5(\mu\text{-}H)_{5-n}(CO)_{20}]^{n-}$ ($n = 0, 1$) reported here fill this gap, at least partially.

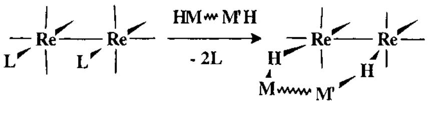
We recently exploited the σ-donor capability of transition metal hydrides[3–5] in the synthesis of open-chain tri- and

---

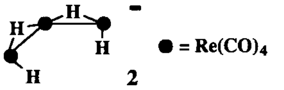
[*] Prof. G. D'Alfonso, Dr. M. Bergamo, Prof. T. Beringhelli
Dipartimento di Chimica Inorganica,
Metallorganica e Analitica e Centro CNR CSSMTBO
Via Venezian 21, I-20133 Milano (Italy)
Fax: (+39) 2-2362748
E-mail: dalf@csmtbo.mi.cnr.it

Dr. M. Moret, Dr. P. Mercandelli, Prof. A. Sironi
Dipartimento di Chimica Strutturale e
Stereochimica Inorganica e Centro CNR CSSMTBO,
Via Venezian 21, I-20133 Milano (Italy)

tetranuclear clusters,[6,7] by allowing hydrido-carbonyl rhenates to react with [$Re_2(CO)_9L$], where L is a very labile ligand such as THF or H_2O (the otherwise labile MeCN ligand is not labile enough to be substituted by neutral[8] or anionic[6] hydride complexes). Recently the di-substituted complex 1,2-*eq,eq*-[$Re_2(CO)_8(THF)_2$] (**1**) was obtained by the reaction of [$Re_2(\mu\text{-}H)_2(CO)_8$] with diazomethane.[9] The success of this reaction suggests that ring clusters could be obtained, as shown in Scheme 1, by reaction with complexes that contain two terminal hydride groups and are therefore able to act as bidentate "ligands". We have prepared one such species, the trinuclear L-shaped anion [$Re_3H_2(\mu\text{-}H)_2(CO)_{12}]^-$ (**2**, Scheme 2), by addition of [$ReH_2(CO)_4]^-$ to [$Re_2(\mu\text{-}H)_2(CO)_8$] in a reaction analogous to the previously reported addition of [$Re(CO)_5]^-$ to [$Re_2(\mu\text{-}H)_2(CO)_8$].[6] The treatment of **1** with a stoichiometric amount of **2** afforded the novel cyclic pentanuclear cluster anion [$Re_5(\mu\text{-}H)_4(CO)_{20}]^-$ (**3**) in high yield as determined spectroscopically [Eq. (1)].



Scheme 1. Synthesis of ring clusters.



2

Scheme 2. The trinuclear, L-shaped anion [$Re_3H_2(\mu\text{-}H)_2(CO)_{12}]^-$ (**2**).

$$\underset{\mathbf{1}}{[Re_2(CO)_8(thf)_2]} + \underset{\mathbf{2}}{[Re_3H_2(\mu\text{-}H)_2(CO)_{12}]^-} \longrightarrow \underset{\mathbf{3}}{[Re_5(\mu\text{-}H)_4(CO)_{20}]^-} + 2\,thf \quad (1)$$

The addition of stoichiometric amounts of CF_3SO_3H to anion **3** in CH_2Cl_2 gave the neutral derivative [$Re_5(\mu\text{-}H)_5(CO)_{20}$] (**4**) in quantitative yield, as shown by IR and NMR spectroscopy.

The metal frameworks of clusters **3**[10] and **4**[13] (80 valence electrons) exhibit an uncommon cyclopentane-like geometry, unprecedented among purely hydrido-carbonyl clusters (Figures 1 and 2). Previous examples of carbonyl compounds with a pentacyclic arrangement of the metal atoms have extra ligands bridging the metal atoms across the ring that contribute to the stabilization of the metallic core; see for example the $Ru_5(\mu_5\text{-}C_2)$ clusters[14a–d] and, particularly significant to the present study, the isoelectronic [$Mn_5(\mu_5\text{-}In)(CO)_{20}]^{2-}$ anion.[14e]

The Re_5 ring in anion **3** and in the two crystallographically independent molecules **4a** and **4b** is built up of five octahedral $Re(CO)_4$ units with local idealized C_{2v} symmetry. Their relative conformations can be described as *e*/*s*/*s*/*s*/*e* (*e* = eclipsed, *s* = staggered) starting from Re1–Re2; the eclipsed Re-H-Re interactions are longer than the staggered ones (see Figures 1 and 2).

The local steric arrangement of the CO groups and the results of potential energy calculations on atom pairs[15] suggest that all the Re-H vectors, in both **3** and **4**, point *inside* the metal ring. This feature was first observed for two of the Re(μ-H)Re interactions in [$Re_4(\mu\text{-}H)_4(CO)_{16}$].[2a] Here *all* the μ-H bridges can lie simultaneously inside the Re_5 moiety because the metallacycle is puckered and not strictly planar as in the cyclobutane analogue.[2a]

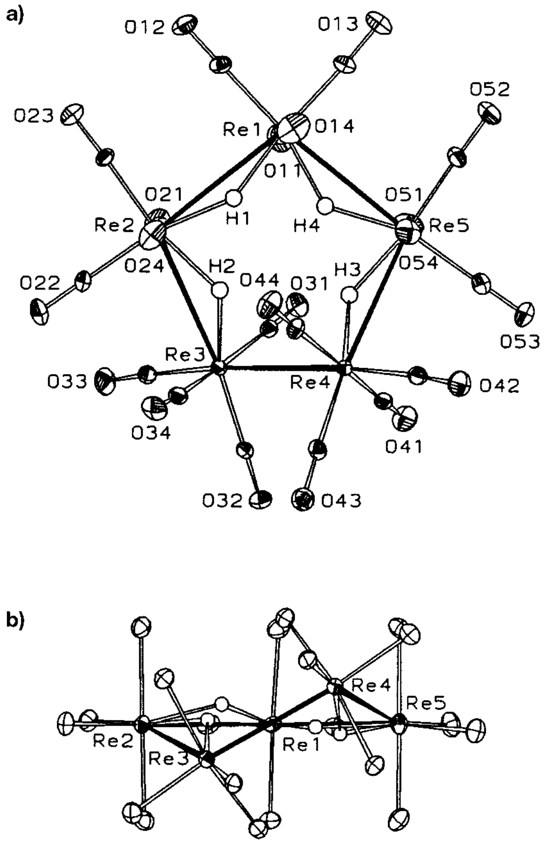


Figure 1. Ortep drawing of anion **3**. a) Top view. b) The same anion viewed along the Re2-Re1-Re5 bisector. Metal-metal bond lengths [Å]: Re1–Re2 3.455(1), Re2–Re3 3.280(1), Re3–Re4 3.086(1), Re4–Re5 3.302(1), Re5–Re1 3.416(1).

Analysis of the ring conformation with the puckering coordinates of Rao et al.[16] gave a twisted conformation on the Re3–Re4 bond for **3** (Figure 1b), with a puckering amplitude $\tau_m = 48.0°$ and a pseudorotation parameter $P = 252.5°$ (calculated from the endocyclic torsion angles and with the bond Re1–Re2 taken as the reference). The resulting anion possesses idealized C_2 symmetry with the twofold axis passing through Re1 and the middle of the unbridged Re3–Re4 edge. The λ conformation of the Re_5 ring is shown in Figure 1b.

One of the two independent molecules in **4** (**4a**) exhibits features similar to **3** (twisted conformation on the Re3–Re4 edge, $\tau_m = 47.2°$, $P = 255.9°$), even though all the Re–Re edges are bridged by hydrogen and longer than in **3** (Re1–Re2 and Re1–Re5 are particularly long; the former is the longest among pure hydrido-carbonyl rhenium complexes). In contrast, in **4b** (Figure 2), the Re_5 ring has an almost envelope conformation on Re4 (Figure 2b) with $\tau_m = 49.8°$ and $P = 262.6°$.[17] A conformational change such as this is associated with rotation about the Re2–Re3 edge. The molecule **4b** has an average C-Re2-Re3-C torsion angle of 32(3)°, which is closer to staggered (45°) than eclipsed (0°).

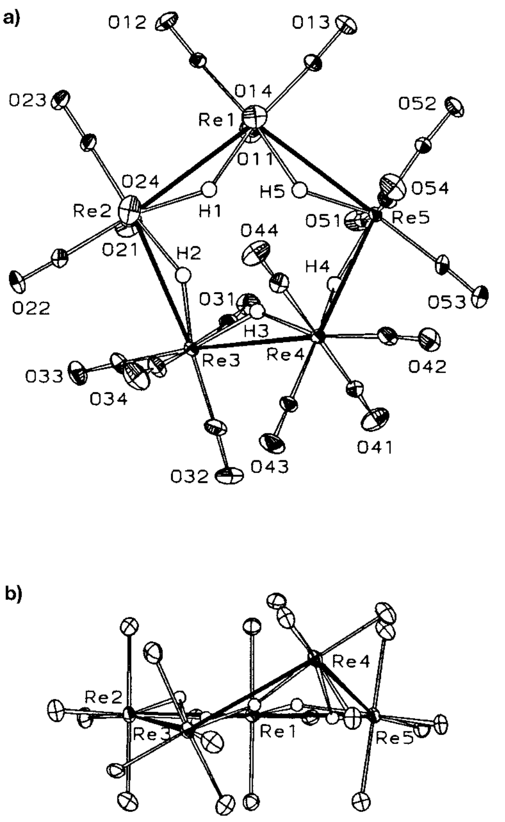


Figure 2. Ortep drawing of **4b**. a) Top view. b) The same molecule viewed along the Re2-Re1-Re5 bisector, to show the envelope conformation. Metal–metal bond lengths (the values for **4a** are given in square brackets) [Å]: Re1−Re2 3.4967(5) [3.4934(5)], Re2−Re3 3.3537(5) [3.3663(5)], Re3−Re4 3.3546(6) [3.3308(6)], Re4−Re5 3.3406(5) [3.3286(5)], Re5−Re1 3.4620(6) [3.4696(6)] (mean Re−Re bond length 3.402 in **4b**, 3.398 in **4a**).

The presence of two significantly different conformations in the same crystal, which are both on the pseudorotation path for pentaatomic rings (the puckering amplitude is almost the same in all the three species **3**, **4a**, and **4b**), stems from the high flexibility of these molecules, so that packing forces are sufficient to drive these clusters into different conformations. In agreement with this, only two sharp resonances for carbonyl groups (axial and equatorial CO groups) were observed in the ^{13}C NMR spectra of **3** and **4** in solution, even at 193 K. For **3**, this also implies fast scrambling of the four H ligands over the five Re−Re bonds.

In spite of the octahedral coordination at the Re centers, the puckering amplitude of these rhenium species is comparable with that observed for organic five-membered rings of tetrahedral carbon atoms.[16] The puckering features therefore make these clusters even more akin to the purely organic cycloalkanes, and further demonstrate that isolobality may lead to more than a purely formal relationship.

Experimental Section

The addition of $[Re_2(\mu\text{-}H)_2(CO)_8]$ (143 mg, 0.240 mmol) to a solution of $[NEt_4][ReH_2(CO)_4]$ (103 mg, 0.240 mmol) in THF at 273 K afforded the trinuclear anion **2** instantaneously, as shown by IR spectroscopy. The solvent was removed under vacuum, and the residue was treated with Et_2O (ca. 10 mL) and filtered. Addition of *n*-hexane gave a yellow precipitate of spectroscopically pure $[NEt_4]$**2** (160 mg, 0.156 mmol, 65% yield). IR (THF): $\tilde{\nu}$(CO) = 2098w, 2067m, 2031w, 2002vs, 1989s, 1970ms, 1929m cm^{-1}; ^{1}H NMR ([D]$_8$THF, 193 K): $\delta = -5.82(2), -16.10(2)$. The $[PPh_4]^+$ salt was prepared in the same way.

A sample of $[NEt_4]$**2** (88 mg, 0.0856 mmol) dissolved in THF was treated at 273 K with a solution of **1** (2 mL, ca. 0.045 M) in THF. The solution was allowed to warm up to room temperature, and was then evaporated to dryness. The residue was dissolved in CH_2Cl_2, and IR spectroscopy showed the fast formation of **3**, which was complete within 10 min. Workup with Et_2O/*n*-hexane afforded 85 mg of spectroscopically pure $[NE_4]$**3** (61% yield). IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2115vw, 2092m, 2053mw, 2028vs, 2005s, 1994sh, 1953ms, 1885mw cm^{-1}; ^{1}H NMR ([D]$_8$THF, 193 K): $\delta = -15.74$; ^{13}C NMR ([D]$_8$THF, 193 K): $\delta = 192.1(1), 187.8(1)$.

A sample of $[NEt_4]$**3** (30 mg, 0.018 mmol) in CD_2Cl_2 was treated with CF_3SO_3H (1.8 μL, 0.020 mmol) at 193 K. The solution changed from yellow-orange to colorless, and IR spectroscopy showed that **4** had formed quantitatively. The solution was filtered through Florosil, concentrated and recrystallized from CH_2Cl_2/*n*-hexane to give colorless crystals of **4**. IR (THF): $\tilde{\nu}$(CO) = 2107m, 2094w, 2038vs, 2013s, 1968mw cm^{-1}; ^{1}H NMR ([D]$_8$THF, 193 K): $\delta = -17.22$; ^{13}C NMR ([D]$_8$THF, 193 K): $\delta = 182.5(1), 180.8(1)$.

Received: February 27, 1998 [Z11530IE]
German version: *Angew. Chem.* **1998**, *110*, 2201–2203

Keywords: carbonyl complexes · clusters · hydrides · isolobal relationship · rhenium

---

[1] R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711.

[2] a) N. Masciocchi, A. Sironi, G. D'Alfonso, *J. Am. Chem. Soc.* **1990**, *112*, 9395; b) M. J. Bennet, W. A. G. Graham, J. K. Hoyano, W. L. Hutcheon, *J. Am. Chem. Soc.* **1972**, *94*, 6232; c) D. K. Huggins, W. Fellmann, J. M. Smith, H. D. Kaesz, *J. Am. Chem. Soc.* **1964**, *86*, 4841.

[3] R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789.

[4] L. M. Venanzi, *Coord. Chem. Rev.* **1982**, *43*, 251.

[5] See also: M. Bergamo, T. Beringhelli, G. D'Alfonso, G. Ciani, M. Moret, A. Sironi, *Inorg. Chim. Acta* **1997**, *259*, 291, and references therein.

[6] M. Bergamo, T. Beringhelli, G. D'Alfonso, G. Ciani, M. Moret, A. Sironi, *Organometallics* **1996,** *15*, 3876.

[7] M. Bergamo, T. Beringhelli, G. D'Alfonso, P. Mercandelli, M. Moret, A. Sironi, *Organometallics* **1997**, *16*, 4129.

[8] A. Albinati, R. M. Bullok, B. J. Rappoli, T. F. Koetzle, *Inorg. Chem.* **1991,** *30*, 1414.

[9] L. Carlucci, G. D'Alfonso, D. M. Proserpio, unpublished results.

[10] a) Crystal data for **3**: $C_{28}H_{24}NO_{20}Re_5$, $M_r = 1625.48$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.880(4)$, $b = 19.548(8)$, $c = 21.580(9)$ Å, $\beta = 101.10(1)^\circ$, $V = 4090(3)$ Å^3 (by least-squares refinement on diffractometer angles of centered reflections with $0 < \theta < 23^\circ$), $Z = 4$, $T = 293$ K, graphite-monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\rho_{calcd} = 2.640$ Mg m^{-3}, $F(000) = 2936$, yellow crystal $0.45 \times 0.27 \times 0.22$ mm, $\mu(Mo_{K\alpha}) = 14.818$ mm^{-1}, absorption correction with SADABS, relative transmission 0.646–1.000, SMART diffractometer, ω scan, frame width 0.3°, maximum time per frame 20 s, $\theta = 1.9$–27.0°, $-12 < h < 12$, $-23 < k < 24$, $-26 < l < 26$, 33719 reflections of which 8132 were independent ($R_{int} = 0.0297$), no crystal decay, solution by direct methods (SIR96)[11] and subsequent Fourier syntheses, anisotropic full-matrix least squares on F_o^2 (SHELX97[12]), hydrogen atoms refined with a riding model, data/parameters = 8132/487, GOF(F_o^2) = 0.995, $R1 = 0.0386$ and $wR2 = 0.0653$ for all data, $R1 = 0.0267$ and $wR2 = 0.0622$ for reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 1.8818P]$ where $P = (F_o^2 + 2F_c^2)/3$, max./min. residual electron density 1.863/−1.588 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101153. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[12] G. M. Sheldrick, SHELXL-97: Program for structure refinement, Göttingen, **1997**.

[13] Crystal data for **4**: $C_{20}H_5O_{20}Re_5$, $M_r = 1496.24$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.316(1)$, $b = 18.511(2)$, $c = 19.431(2)$ Å, $\alpha = 77.12(1)$, $\beta = 88.17(1)$, $\gamma = 85.69(1)^\circ$, $V = 3256.9(6)$ Å^3 (by least-squares refinement on diffractometer angles of centered reflections with $0 < \theta < 23^\circ$), $Z = 4$, $T = 293$ K, graphite-monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\rho_{calcd} = 3.051$ Mg m^{-3}, $F(000) = 2640$, colorless crystal $0.28 \times 0.08 \times 0.06$ mm, $\mu(Mo_{K\alpha}) = 18.592$ mm^{-1}, absorption correction with SADABS, relative transmission 0.480–1.000, SMART diffractometer, ω scan, frame width 0.3°, maximum time per frame 40 s, $\theta = 2.2-28.3^\circ$, $-12 < h < 12$, $-24 < k < 24$, $-25 < l < 25$, 37916 reflections of which 14444 were independent ($R_{int} = 0.0379$), crystal decay 1.1 %, solution by direct methods (SIR96)[11] and subsequent Fourier syntheses, anisotropic full-matrix least squares on F_o^2 (SHELX97),[12] hydrogen atoms refined with a riding model, data/parameters = 14444/811, GOF(F_o^2) = 0.789, $R1 = 0.0445$ and $wR2 = 0.0446$ for all data, $R1 = 0.0240$ and $wR2 = 0.0427$ for reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0128P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, max./min. residual electron density 1.080/−1.208 e Å^{-3}.[10b]

[14] a) C. J. Adams, M. I. Bruce, B. W. Skelton, A. H. White, *J. Chem. Soc. Chem. Commun.* **1992**, 26; b) C. J. Adams, M. I. Bruce, B. W. Skelton, A. H. White, *Chem. Commun.* **1996**, 969; c) C. J. Adams, M. I. Bruce, B. W. Skelton, A. H. White, *Chem. Commun.* **1996**, 975; d) C. J. Adams, M. I. Bruce, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1996**, *506*, 191; e) M. Schollenberger, B. Nuber, M. L. Ziegler, *Angew. Chem.* **1992**, *104*, 329; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 350.

[15] A. G. Orpen, *J. Chem. Soc. Dalton Trans.* **1980**, 2509.

[16] S. T. Rao, E. Westhof, M. Sundaralingam, *Acta Crystallogr. Sect. A* **1981**, *37*, 421.

[17] For comparison: $[Mn_5(\mu_5\text{-}In)(CO)_{20}]$[14e] yields puckering values of $\tau_m = 46.9^\circ$ and $P = 99.2^\circ$, which correspond to an envelope conformation.

Photoluminescent Rigid Molecular Rods with Cumulenic C_n ($n = 3, 4$) Spacers: Modulation of Electronic Interaction**

Bo Hong* and Jeffrey V. Ortega

Rigid molecular rods with linear structures, molecular wires, are currently studied as important components for the construction of functional nanoscale photonic and electronic devices.[1,2] With the incorporation of photoactive and/or redox-active metal centers, these molecular assemblies may present interesting properties based on long range electron/energy transfer and electronic communication between the two remote ends of the wires.[2–5] To ensure the directionality and also to construct multicomponent supramolecular systems with well-defined structures, rigid spacers must be used to afford restricted conformational mobility and a controllable distance between structural subunits. In addition, spacers (for example, polyphenyls,[6] alkenes,[7] or alkynes[5,8]) can also be selected to serve as electron-conducting active components to promote long-range electronic coupling between terminal subunits or (for example, saturated hydrocarbons[9]) to serve as passive connecting components.

Systems with unsaturated sp carbon chains (C_n) between two subunits constitute one of the most fundamental classes of one-dimensional molecular wires, however, intense studies in numerous laboratories have focused on the systems with alkynes or acetylenyl bridges.[2,5,8] We report here the photoluminescent and redox-active systems with Ru and Os centers spanned by allene (C_3) or cumulene (C_4) bridges, and the preliminary data on the unique molecular photophysical and redox properties of these new rigid rodlike supramolecular systems. The unique structures of the allene and cumulene bridges permit the tuning of electronic communication between the end subunits. In the C_3 chain the two terminal pπ orbitals will be rotated by 90°, while in the C_4 chain the terminal pπ orbitals remain conjugated (Figure 1).

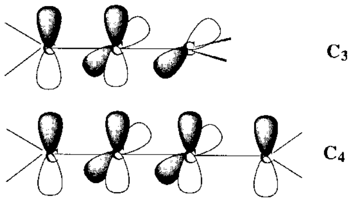


Figure 1. Comparison of the pπ orbitals in the C_3 and C_4 bridges.

As a result, the electronic coupling across the sp carbon chain can be readily controlled by changing the number of carbon atoms.

The C_n-bridged tetratopic spacers, namely, 1,1′,3,3′-tetrakis(diphenylphosphanyl)allene (C_3P_4), 1,1′,4,4′-tetrakis(diphenylphosphanyl)cumulene (C_4P_4), and the ligand 1,1′-bis(diphenylphosphanyl)ethene (C_2P_2e) are prepared according to the literature methods.[10–12] The use of the phosphane group in the spacer here has two advantages. First, it serves as a linker group between the C_n bridge and the metal-based subunits ($M(bpy)_2$ (M = Ru and Os; bpy = 2,2′-bipyridine)). Second, the incorporation of phosphane ligands in polypyridyl-osmium(II) complexes can enhance the lifetime of the ^{3}MLCT state;[13–15] the replacement of one of the σ-donating polypyridyl ligands with phosphane can result in the increase in the energy of the ^{3}MLCT excited state and the decrease of the rate of nonradiative decay.

The PF_6^- salts of the C_n-bridged ruthenium(II) and osmium(II) complexes are synthesized by treatment of C_nP_4 ($n = 3$ or 4), in a refluxing tetrahydrofuran/ethylene glycol mixture, with $[M(bpy)_2Cl_2]$ (M = Ru or Os, Table 1). Mono- or bimetallic complexes, MC_2P_2e, MC_nP_4 ($n = 3$ or 4), and MC_nP_4M ($n = 3$ or 4), are obtained by using different metal-to-ligand ratios. All new complexes have been fully characterized by $^{31}P\{^1H\}$ NMR spectroscopy, fast atom bombardment mass spectrometry (FAB-MS), and elemental analysis. Specifically, many of the fragment ions observed in FAB-MS only involve sequential loss of counteranions (PF_6) and PPh_2 units, and the inner sphere metal–ligand coordination was left intact, thus making peak identification straightforward.

---

[*] Prof. B. Hong, J. V. Ortega
Department of Chemistry
University of California, Irvine
Irvine, CA 92697-2025 (USA)
Fax: (+1)714-824-3168
E-mail: bhong@uci.edu

[**] This work was supported by the University of California, Irvine, UCI's Physical Sciences Committee on Research, and the US National Science Foundation CAREER Award (CHE-9733546). J.V.O. acknowledges support from the Graduate and Professional Opportunity Program from the US Department of Education.

1433-7851/98/3715-2131 $ 17.50+.50/0