

Dalton Communications

Rhenium–Iridium Clusters *via* Addition of $[\text{Ir}(\text{CO})_4]^-$ to $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ Tiziana Beringhelli,^a Gianfranco Ciani,^b Giuseppe D'Alfonso,^{*a} Luigi Garlaschelli,^a Massimo Moret^b and Angelo Sironi^{*b}^a Dipartimento di Chim. Inorg. e Metallorganica, Via G. Venezian 21, 20133 Milano, Italy^b Istituto di Chimica Strutturistica Inorganica, Via G. Venezian 21, 20133 Milano, Italy

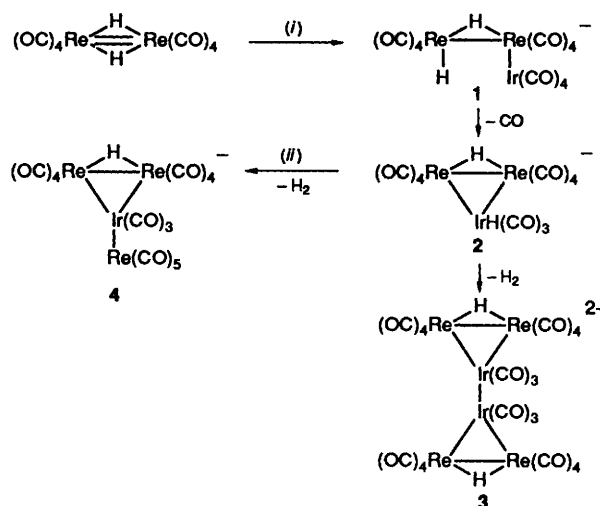
The unsaturated molecule $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ adds $[\text{Ir}(\text{CO})_4]^-$ at -80°C to give the anion $[(\text{OC})_4\text{HRe}(\mu\text{-H})\text{Re}(\text{CO})_4\text{Ir}(\text{CO})_4]^-$, which at higher temperatures transforms into the triangular cluster $[\text{Re}_2\text{IrH}_2(\text{CO})_{11}]^-$; the latter, by reductive coupling with itself or with $[\text{ReH}(\text{CO})_5]$, affords $[\{\text{Re}_2\text{Ir}(\mu\text{-H})(\text{CO})_{11}\}_2]^{2-}$ and $[\text{Re}_3\text{Ir}(\mu\text{-H})(\text{CO})_{16}]^-$, respectively, which have been characterized by X-ray diffraction.

Rational approaches to the synthesis of mixed-metal clusters are at present being actively pursued, in connection with the interest in polymetallic catalysts.¹ A well established method is the addition of a carbenoid fragment, as such PtL_2 , to ethylene-like molecules, leading to trimetallacyclopropane clusters.² In this context we have previously reported the reactions of the unsaturated molecule $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ with $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]^3$ and with $[\text{Pt}(\text{cod})_2]$ (cod = cycloocta-1,5-diene)⁴ which afford $[\text{Re}_2\text{Pt}(\mu\text{-H})_2(\text{CO})_8\text{L}_2]$ (L = PPh_3 , $\text{L}_2 = \text{cod}$) triangular clusters. We have now investigated the reactivity of the same unsaturated molecule with a pseudo-halide species, $[\text{Ir}(\text{CO})_4]^-$.

The addition of $[\text{Ir}(\text{CO})_4]^-$ to $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ at -80°C gives the trimetallapropene anion $[(\text{OC})_4\text{HRe}(\mu\text{-H})\text{Re}(\text{CO})_4\text{Ir}(\text{CO})_4]^-$ **1** (Scheme 1),[†] in a reaction similar to the addition of H^- to $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ affording $[(\text{OC})_4\text{HRe}(\mu\text{-H})\text{ReH}(\text{CO})_4]^-$,⁵ in line with the isolobality between $[\text{Ir}(\text{CO})_4]$ and H^- .⁶ Pseudohalide anions, such as $[\text{Ir}(\text{CO})_4]^-$, are quite common and therefore this approach to heteronuclear metal-metal bond formation could be widely applicable.

On raising the temperature to -20°C evolution of CO occurs and the hydridic resonances of compound **1** are replaced by a new couple of signals, ratio 1:1,[‡] suggesting formation of the triangular cluster $[\text{Re}_2\text{IrH}_2(\text{CO})_{11}]^-$ **2** (Scheme 1), where the ring closure has been promoted by CO loss and hydrogen atom transfer to the Ir. Attempts to grow crystals of **2**, even at -20°C , resulted in the isolation of a different species, $[\{\text{Re}_2\text{Ir}(\mu\text{-H})(\text{CO})_{11}\}_2]^{2-}$ **3**, the X-ray crystal structure analysis of which (as $[\text{NEt}_4]^+$ salt) confirmed the proposed structure for **2**.[§] The $[\{\text{Re}_2\text{Ir}(\mu\text{-H})(\text{CO})_{11}\}_2]^{2-}$ anion (Fig. 1) has a novel cluster shape consisting of two triangles joined by an Ir–Ir bond, which clearly originates from the dimerization of **2**, *via* elimination of H_2 (Scheme 1).

The lability of compound **2** toward intermolecular H coupling has been further verified in the reaction with $[\text{ReH}(\text{CO})_5]$ (Scheme 1), which affords, slowly but in high yields,[¶] the

Scheme 1 (i) $[\text{Ir}(\text{CO})_4]^-$; (ii) $[\text{ReH}(\text{CO})_5]$

[§] Crystal data for compound **3**: $\text{C}_{38}\text{H}_{42}\text{Ir}_2\text{N}_2\text{O}_{22}\text{Re}_4$; $M = 2008.0$, monoclinic, space group $P2_1/c$ (no. 14), $a = 20.303(6)$, $b = 12.523(3)$, $c = 20.367(5)$ Å, $\beta = 90.51(2)^\circ$, $U = 5178(4)$ Å³, $F(000) = 3656$, $Z = 4$, $D_c = 2.57$ g cm⁻³, Mo-K α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 146.2$ cm⁻¹, crystal dimensions $0.15 \times 0.15 \times 0.20$ mm. Intensities were measured with a CAD4 automatic diffractometer at room temperature with θ ranging from 3 to 23.5° ; data were corrected for absorption (maximum, minimum relative transmission factors 1.00, 0.60), Lorentz-polarization effects and decay. 2213 Reflections with $I > 3\sigma(I)$ were used in the structure refinements. The hydrido ligands were placed in idealized positions on the basis of the experimental heavy-atom stereochemistry, using atom-pair-potential computations. The final R value was 0.040 ($R' = 0.039$), weighting scheme $w = 4|F_o|^2/\sigma^2(|F_o|^2)$, $\sigma(|F_o|^2) = [\sigma^2(I) + (pI)^2]^{1/2}/L_p$, $p = 0.035$.

[¶] Compound **2** (generated in a NMR tube by dissolving in $[\text{D}_2\text{H}_8]$ tetrahydrofuran at -80°C $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ (18 mg, 0.03 mmol) and $[\text{NEt}_4][\text{Ir}(\text{CO})_4]$ (13 mg, 0.03 mmol), and then raising the temperature to -20°C) was treated with $[\text{ReH}(\text{CO})_5]$ (8 μl , ca. 0.054 mmol). After 14 d at -20°C , NMR monitoring showed the complete consumption of the reagents, with **4** and $[\text{Re}_2(\text{CO})_{10}]$ (IR analysis) being the only products present. Other, as yet unidentified, species have been observed at intermediate reaction times.

[†] A solution of $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]$ (21 mg, 0.035 mmol) in $[\text{D}_2\text{H}_8]$ tetrahydrofuran was treated in an NMR tube at -80°C with $[\text{NEt}_4][\text{Ir}(\text{CO})_4]$ (15 mg, 0.035 mmol), causing the quantitative and instantaneous formation of **1**, exhibiting two resonances attributable to a terminal and a bridging H ligand ($\delta -5.5$ and -16.15 , $J_{\text{HH}} 3.2$ Hz). No evolution of CO or H_2 was revealed by gas chromatographic analysis.

[‡] Compound **2**: IR $\nu(\text{CO})$ 2044m, 2016m, 1980s, 1946mw and 1911m cm⁻¹; NMR $\delta -12.8$ and -17.9 . Compound **3**: IR $\nu(\text{CO})$ 2060m, 2037s, 1992vs, 1942mw and 1909s cm⁻¹; NMR $\delta -18.3$. Compound **4**: IR $\nu(\text{CO})$ 2015w, 2065m, 2046ms, 2001vs, 1950m and 1913m cm⁻¹; NMR $\delta -18.2$.

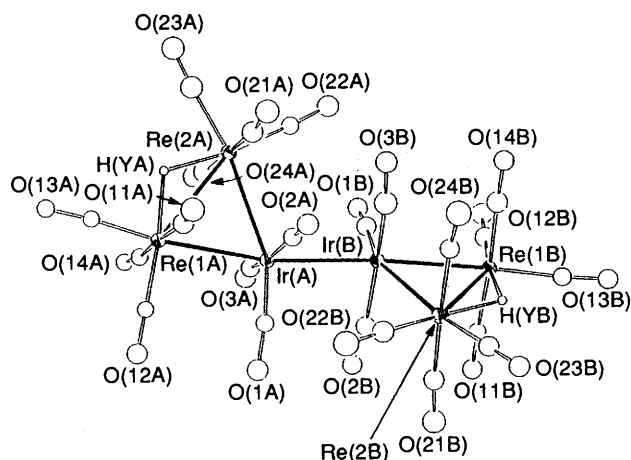


Fig. 1 The structure and labelling scheme for the $[\{\text{Re}_2\text{Ir}(\mu\text{-H})(\text{CO})_{11}\}_2]^{2-}$ anion **3** viewed along the idealized C_2 symmetry axis bisecting the Ir-Ir bond. Relevant bond lengths are: Ir(A)-Ir(B) 2.891(2), Ir(A)-Re(1A) 2.885(2), Ir(A)-Re(2A) 2.956(2), Ir(B)-Re(1B) 2.896(2), Ir(B)-Re(2B) 2.951(2), Re(1A)-Re(2A) 3.118(2) and Re(1B)-Re(2B) 3.095(2) Å

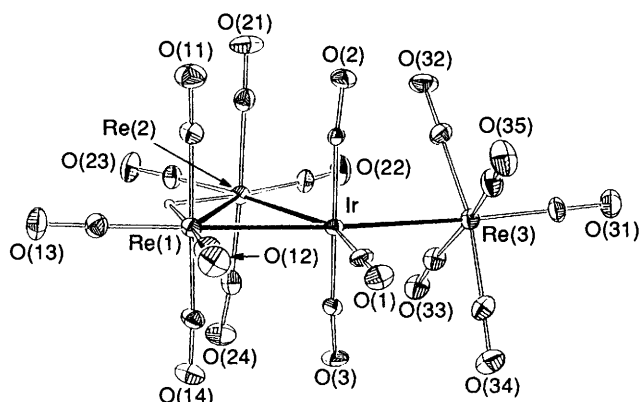


Fig. 2 The structure and labelling scheme for the $[\text{Re}_3\text{Ir}(\mu\text{-H})(\text{CO})_{16}]^-$ anion **4**. Relevant bond lengths for molecules A and B (in square brackets): Ir-Re(1) 2.897(1) [2.901(1)], Ir-Re(2) 2.952(1) [2.957(1)], Ir-Re(3) 2.933(1) [2.938(1)] and Re(1)-Re(2) 3.119 [3.124(1)] Å

'methylcyclopropane' species $[\text{Re}_3\text{Ir}(\mu\text{-H})(\text{CO})_{16}]^-$ **4**, whose structure has been determined by X-ray analysis (Fig. 2).^{*} This 'reductive coupling' of suitable HML_n species closely resembles the condensation between hydrido and alkyl complexes, with alkane elimination, widely used to form heteronuclear metal-metal bonds.¹

The series of clusters reported here nicely illustrates the stepwise growth of the iridium-metal interactions at the expense of the iridium-ligand ones, while the iridium centre becomes sequentially isolobal to CH_3 , CH_2 and CH [*i.e.* $\text{Ir}(\text{CO})_4$, $\text{IrH}(\text{CO})_3$ and $\text{Ir}(\text{CO})_3$].

* Crystal data for compound **4**: $\text{C}_{24}\text{H}_{21}\text{IrNO}_{16}\text{Re}_3$, $M = 1330.2$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), $a = 14.482(1)$, $b = 13.511(2)$, $c = 34.534(4)$ Å, $\beta = 98.63(1)^\circ$, $U = 6681(2)$ Å³, $F(000) = 4816$, $Z = 8$, $D_c = 2.65$ g cm⁻³, Mo-K α radiation, $\mu(\text{Mo-K}\alpha) = 150.1$ cm⁻¹, crystal dimensions 0.10 × 0.20 × 0.20 mm. Intensities were measured (θ 3–25°) and the data were corrected (maximum, minimum relative transmission factors, 1.00, 0.55) as for **3**. 5594 Reflections with $I > 3\sigma(I)$ were used in the structure refinements. The hydrido ligands were placed in idealized positions as before. The final R value was 0.030 ($R' = 0.032$), weighting scheme as for **3**.

Atomic coordinates, thermal parameters and bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

Compounds **3** and **4** share the presence of a spiked-triangular $\text{Re}_2\text{Ir}(\mu\text{-H})(\text{CO})_{11}\text{M}_s$ moiety (where M_s indicates a variably substituted metal), characterized by eleven (six axial and five equatorial) CO ligands, a hydride spanning the Re-Re edge and an (equatorial) spike M_s on the Ir atom. Noteworthy the spike is slightly off the triangular plane and has a staggered conformation (the dihedral angles between the proper substituents on Ir and M_s are close to 45°). Moreover, within the triangle, the Re-Ir interaction *trans* to M_s (average on four fragments 2.895 Å) is systematically shorter than the *cis* one (average 2.954 Å). The shortening of the M-M bond *trans* to the spike M_s observed in $\text{Os}_3(\text{CO})_{11}\text{M}_s$ [$\text{M}_s = \text{Os}(\text{CO})_4\text{L}$; $\text{L} = \text{P}(\text{OCH}_2)_3\text{-CMe}_2$,⁷ Bu^+NC ,⁸ or PMe_3]⁹ was related to the weak donor ability of the M_s ligand (a 18-electron species). On the other hand, the bulky fragment M_s could lengthen the *cis* M-M interaction, as thoroughly analysed in $\text{M}_3(\text{CO})_{11}\text{L}$ derivatives ($\text{M} = \text{Os}$ or Ru ; $\text{L} =$ phosphines, phosphites or arsines).¹⁰

Very few Re-Ir mixed-metal complexes have been reported until now and they are mainly dinuclear, containing bridged metal-metal interactions.¹¹ The only known unsupported Re-Ir bonds are found in the complexes $[\{\text{Re-C}(\text{CO})_{21}\}\text{Ir}(\text{L}'\text{L}')^{2-}$ ($\text{L} =$ olefin, $\text{L}' = \text{CO}$)¹² and in the linear $[\{\text{Re}(\text{CO})_5\}_2\text{Ir}(\text{CO})_3\text{H}]$ ¹³ (average Re-Ir 2.879 Å in the former and 2.914 Å in the latter species), while in **4** the spike Ir-Re bond is 2.935 Å (average). Thus, even if the lack of a neat reference value for the Re-Ir bond distance does not allow a clear differentiation between *trans* influence (of the Ir- M_s bond) and steric effects (of the bulky M_s), it seems reasonable to consider steric effects to be dominant in determining the spiked-triangle conformation.

Acknowledgements

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