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Preliminary communication

SYNTHESIS OF TWO NOVEL Re_7 CARBIDO-CARBONYL COMPLEXES. X-RAY CRYSTAL STRUCTURE OF THE ANION $[Re_7C(CO)_{22}]^-$

T. BERINGHELLI, G. D'ALFONSO *, M. DE ANGELIS,
Dipartimento di Chimica Inorganica e Metallorganica, Via Venezian 21, 20133 Milano (Italy)

G. CIANI and A. SIRONI*
Istituto di Chimica Strutturistica Inorganica, Via Venezian 21, 20133 Milano (Italy)

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Summary

Oxidation of the carbido cluster trianion $[Re_7C(CO)_{21}]^{3-}$ with $C_7H_7BF_4$ gives the unstable paramagnetic species $[Re_7C(CO)_{21}]^{2-}$, which, under an atmosphere of CO undergoes further oxidation to the monoanion $[Re_7C(CO)_{22}]^-$. This anion, which was characterized by an X-ray study, has the unusual feature of a CO ligand bridging a Re–Re edge.

We are currently studying the reactivity toward electrophiles of the trianion $[Re_7C(CO)_{21}]^{3-}$ (compound **1**), which contains a monocapped octahedral skeleton of Re atoms centered on a carbide atom, and was the first member of the rapidly growing family of carbido-carbonyl clusters of rhenium [1]. Iodine in acetonitrile causes degradation of this cluster [2], while H^+ and the cations M^+ of the IB group give addition reactions [3]. We report here on the reaction with a different type of electrophile, the cycloheptatrienylium (tropylium) cation.

Addition of 1 equivalent of $C_7H_7BF_4$ to a solution of $[P_2Ph_6N]_3[Re_7C(CO)_{21}]$ in anhydrous CH_2Cl_2 * under N_2 at room temperature caused a rapid darkening of the solution. After 30 min, IR monitoring showed that the ν(CO) bands of **1** had disappeared and then replaced by bands shifted about 25 cm^{-1} to higher frequency (1993vs, 1923mw and 1880sh cm^{-1}). No CO evolution was revealed by GLC analysis. The ESR spectra at −150°C of the frozen solution and of the solid residue obtained by removing the solvent both showed a strong broad resonance at

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* The use of non protic and carefully dried solvents was necessary to avoid the reversible reaction $C_7H_7^+ + ROH \rightleftharpoons C_7H_7OR + H^+$ [4], which leads to formation of the hydride $[Re_7HC(CO)_{21}]^{2-}$ [3], as spectroscopically observed in methanol or in wet acetone.

$g = 2.35$. These observations are consistent with the occurrence of a simple monoelectronic oxidation to a paramagnetic (97 valence electrons) species $[Re_7C(CO)_{21}]^{2-}$ (compound **2**). Although many reactions of rhenium carbonyl cluster anions with oxidizing agents (including the tropylium ion [5]) have been studied, this is the first time that oxidation to a paramagnetic species has been observed. The compound is air sensitive, and unstable in protic solvents, and attempts to obtain it as a pure solid resulted in extensive decomposition. Treatment of a THF solution of **2** with sodium amalgam rapidly regenerated the parent trianion.

Addition to compound **2** of a further equivalent of the tropylium salt in anhydrous CH_2Cl_2 did not cause any immediate reaction. Under CO, however, a second oxidation, accompanied by CO addition, rapidly occurred, to give high yields of the new compound $[Re_7C(CO)_{22}]^-$ (**3**) (ν(CO) 2080vw, 2032vs, 2018s, 2005sh, 1995sh, 1950mw, 1910w, 1850vw cm^{-1}), which was characterized by an

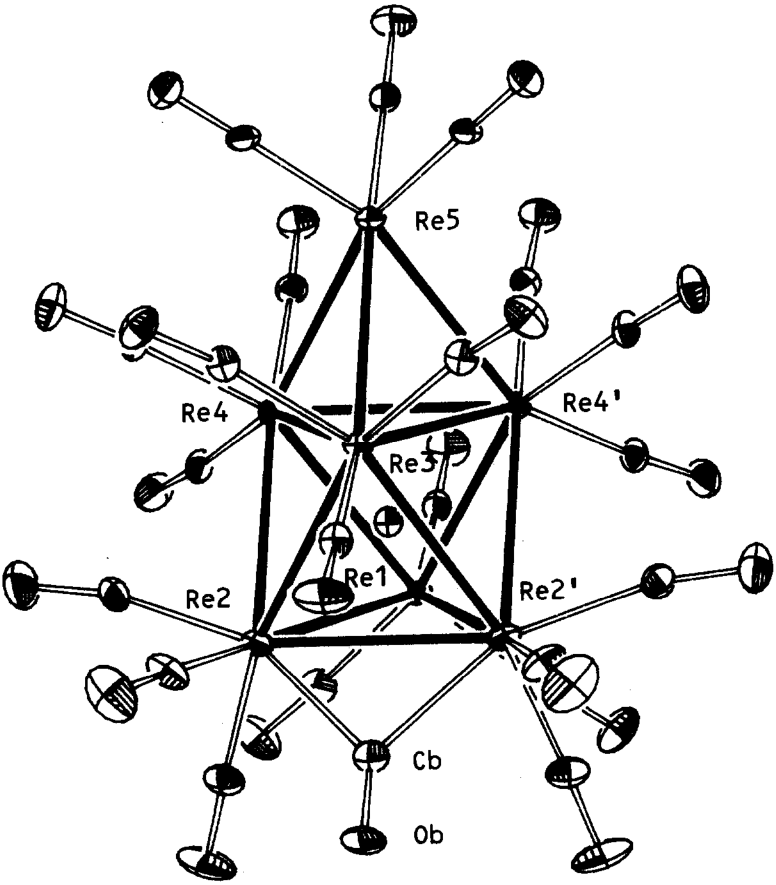
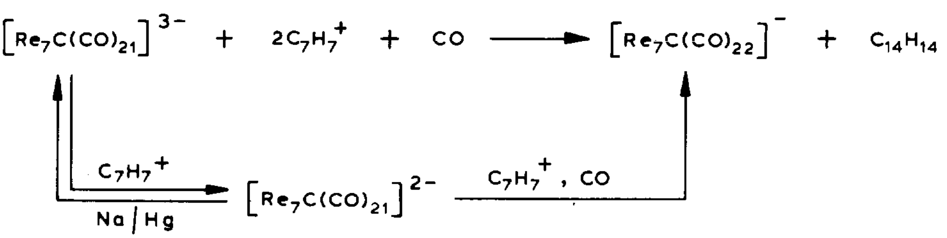


Fig. 1. A view of the $[Re_7C(CO)_{22}]^-$ species. The Re–Re bond distances are: 1–2 3.058, 1–4 2.970, 2–2′ 2.973, 2–3 2.994, 2–4 3.050, 3–4 2.950, 3–5 2.926, 4–4′ 2.986, 4–5 3.005 Å, the e.s.d.s being of 0.001 Å. Re–$C_{carbide}$ (mean) 2.12(1), Re–$C_{bridging\ CO}$ 2.19(1) Å.



SCHEME 1.

X-ray diffraction study of the NEt_4^+ salt *. The same product can be more conveniently obtained directly from **1** by use of 2 equiv. of the tropylium salt under CO.

Similar reactions leading to the replacement of two negative charges by a CO ligand have been previously reported (see for instance ref. 6). In the present work we have demonstrated the occurrence of the two step process shown in Scheme 1.

The structure of the anion **3** is shown in Fig. 1. It possesses a crystallographic imposed *Cs* symmetry (the mirror plane passing through Re(5), Re(3), Re(1) and the carbide) and contains the highest number of carbonyl ligands ever observed in a M_7 compact cluster complex. One of the CO groups is double bridging on a Re–Re edge of the basal non-capped triangle, a rare finding in rhenium complexes chemistry. [7]

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* *Crystal data.* $C_{31}H_{20}NO_{22}Re_7$, $M = 2061.9$, monoclinic, a 9.763(2), b 13.958(3), c 15.453(2) Å, β 90.66(1)°, U 2105.7 Å^3, D_c 3.25 g cm^{-3}, $Z = 2$, $F(000) = 1828$, space group $P2_1/m$ (No. 11), λ(Mo-K_α) 0.71073 Å, μ(Mo-K_α) 203.97 cm^{-1}. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, on the basis of 2587 significant ($I > 3\sigma(I)$) data, up to a current R value of 0.028.
A table of atomic coordinates and a full list of bond lengths and angles has been deposited with the Cambridge Crystallographic Data Centre.