09.5-5   SYNTHESIS, X-RAY STRUCTURE AND ELECTROCHEMISTRY OF [Pd$_3$(μ-CO)$_2$(C$_5$Me$_5$)$_3$] [CF$_3$SO$_3$]. By N. Boag, D. Boucher, J.A. Davies, A.A. Pinkerton and R. Syed, Department of Chemistry, University of Toledo, Toledo, Ohio 43606, U.S.A. and Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England.

Protonation of [Pd$_2$(μ-CO)$_2$(C$_5$Me$_5$)$_2$] (eg with HBF$_4$ or HSO$_3$CF$_3$) in diethyl ether solution leads to formation of [Pd$_3$(μ-CO)$_2$(C$_5$Me$_5$)$_3$][X] (X = BF$_4$, SO$_3$CF$_3$). IR spectroscopy confirms the presence of bridging carbonyls and a non-coordinated anion. Where X = SO$_3$CF$_3$ the X-ray structure has been solved. Data are as follows: H$_{45}$Pd$_3$C$_{33}$F$_3$O$_5$S, M$_r$ = 929.98, monoclinic, P2$_1$/m, a = 8.440(2), b = 20.867(5), c = 10.806(2)Å, β = 108.81(2)°, V = 1801.5Å^3, z = 2, D$_x$ = 1.71 gcm^{-3}, λ(Mo K$_\alpha$) = 0.71073Å, μ = 15.7 cm^{-1}, F(000) = 928, T$^\alpha$ = 21(1)°C, R$_2$ = 0.032 for 3112 unique reflections with F^2 > 3σ(F^2) of 3645 total unique data. The structure consists of an approximately equilateral triangle of Pd atoms (mean Pd-Pd = 2.62Å; mean Pd-Pd-Pd = 59.97°) with the two faces of the triangle capped by triply bridging carbonyls and the three corners capped by η^5-C$_5$Me$_5$ ligands. The CF$_3$SO$_3$$^-$ ion exhibits disorder. This Pd$_3$$^+$ cluster, with 26 metal valence electrons, is closely related to the neutral Ni$_3$ analog (27 valence electrons) first prepared by Fischer and Palm (Chem.Ber. 1958, 91, 1725) and the CoNi$_2$(26 valence electrons), CoNi$_2$$^-$ (27 valence electrons) and Ni$_3$$^-$ (28 valence electrons) clusters studied by Dahl et al. (J. Am. Chem. Soc. 1982, 104, 3054). Cyclic voltammograms of the 26 valence electron Pd$_3$$^+$ cluster measured in 0.1M tetra (n-butyl)ammonium perchlorate in dichloromethane at a Pt working electrode at a scan rate of 200 mV s^{-1} reveal two discrete redox processes. A reversible reduction is encountered at -0.43 V vs. Ag/AgCl (Ep(a)-Ep(c) = 80mV; i$_c$/i$_a$ = 1.05)and a second less reversible reduction at -1.22 V (Ep(a)-Ep(c) = 97mV; i$_c$/i$_a$ = 2.28). These data may imply a facile electrochemical interconversion of cationic, neutral and anionic Pd$_3$ clusters with 26, 27 and 28 metal valence electrons respectively.

09.5-6   STRUCTURAL VARIATIONS OF BRIDGED Re-Re BONDS IN SOME ORGANOMETALLIC COMPOUNDS. By Hans-Jürgen Haupt and U. Flörke, Anorganische und Analytische Chemie, Universität-GH, Warburger Str. 100, D-4790 Paderborn, FRG. H. Preut, Universität Dortmund, FRG.

Coordination compounds with a covalent metal-metal bond are distinguished in first order one without a bridging atom or group and second order one with such a bridging. According to the last-named type the hitherto known metal-metal bond lengths exhibit considerable elongation and shortening related to the corresponding metal-metal single bond length in the unbridged compound. It is therefore difficult to decide whether or not such a metal-metal bond exists. To support the bond, an analysis of structural parameters is necessary besides assumptions due to Extended MO calculations and other measurements.

This contribution represents the influence of various bridging atoms and different coordination spheres for the Re-Re bonded central atoms in the following series of organorhenium compounds (L = PR$_3$, R = C$_6$H$_5$):

Re$_2$(CO)$_{8-n}$L$_n$(μ-H)[μ-PR$_2$][n=1,(I); n=2(II)], Re$_2$(CO)$_8$(μ-PR$_2$)$_2$(III), Re$_3$(CO)$_9$[μ-PR$_2$]$_3$(IV), Re$_2$(CO)$_8$[μ-GaRe(CO)$_5$]$_2$(V), Re$_2$(CO)$_6$L$_2$(μ-GaI$_2$) (μ-I)(VI), Re$_2$(CO)$_4$(μ-I)$_2$(μ-GaRe(CO)$_4$L)(VII), Re$_3$(CO)$_6$L$_3$(μ-Cl)$_3$(μ-GaRe(CO)$_4$L)(VIII),Re$_4$(CO)$_{12}$$^-$($\mu$-GaRe(CO)$_4$L)$_4$(IX).
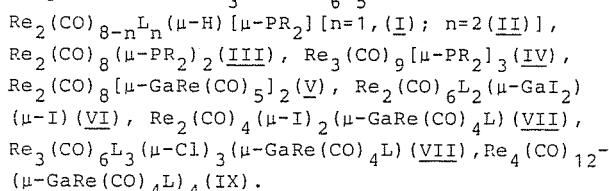
Their molecular structure have been determined by X-ray investigations and crystal data and selected bond length and bond angles are given in the following table I. The relevant structural factors for the change of the Re-Re bond including packing forces and other features will be discussed.

Table I

	S.G.	Core Re$_n$(μ-X)	d(Re-Re) (Å) Re-(μ-X)-Re(°)	Ref.
(I),(II)	P2$_1$/n	n = 2	3.152(1), 3.194(1)	[1]
		X = H,P	81.6(1) , 83.4(1)	
(III)	P2$_1$/n	2	3.928(1)	
		P,P	102.6(1)	[2]
(IV)	P2$_1$/a	3	2.917(4)av.	
		P	73.9(5) av.	[3]
(V)	I4$_1$/a	2	3.139(3)	[4]
		Ga,Ga	74.4(1)	
(VI)	P2$_1$/n	2	3.158(1)	
		Ga,I	70.8(1), 69.6(1)	[2]
(VII)	P1̄	2	2.925(1)	
		Ga,I,I	70.8(1), 62.7(1) av.	[5]
(VIII)	P1̄	3	3.185(4) av.	[2]
		Ga,Cl	72.7(2), 79.6(4)	
(IX)	P1̄	4	2.965(7) av.	[2]
		Ga	67.5(6)	

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[5] Acta Cryst. C 42 (1986), 275.