

are responsible for the relatively low k_{OTs} . Studies on this question and on other low and high k_{OTs}/k_{Br} ratios in vinylic systems are continuing.

Acknowledgment. We are indebted to the Volkswagen Foundation for support of this work and to Professor P. v. R. Schleyer for discussions and comments.

vinyl is more favorable than to ethyl, while Br attachment to vinyl is *less* favorable than to ethyl: L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 6531 (1973). However, the small difference between the solvolysis rates of system 2 and the corresponding fluorenylidene derivatives^{7a} argues against high contribution of this effect.

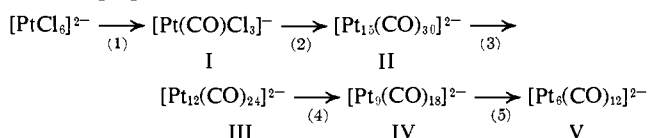
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Synthesis and Structural Characterization of Platinum Carbonyl Cluster Dianions, $[Pt_3(CO)_3(\mu_2-CO)_3]_n^{2-}$ ($n = 2, 3, 4, 5$). A New Series of Inorganic Oligomers¹

Sir:

We wish to report the preparation and structures of a new series of platinum carbonyl cluster dianions of general formula $[Pt_3(CO)_3(\mu_2-CO)_3]_n^{2-}$ ($n = 2, 3, 4, 5$). These species are of particular interest in that they not only give rise to new kinds of metal cluster geometries formally derived by tinker-toy construction from a basic $M_3L_3(\mu_2-X)_3$ -type building block through direct metal-metal interactions but more importantly they also represent an approach to the synthesis of a unique type of unidimensional metal cluster polymer with desirable conductivity properties.

These anions can be prepared either from the reduction of $Pt(CO)_2Cl_2$ with alkali metals in the presence of carbon monoxide or more simply from the reduction of sodium hexacholoplatinate(IV) with carbon monoxide and methanolic sodium hydroxide at atmospheric pressure and room temperature. This latter method of synthesis is analogous to that used in the preparation² of polynuclear rhodium complexes, and the products isolated are similarly dependent upon the amount of added sodium hydroxide. The sequence below shows the dianions *isolated* with increasing concentration of reducing agent.



Step 2 of the overall reaction involves the formation of several intermediates including an insoluble platinum dicarbonyl polymer³ and $[Pt_3(CO)_6]_n^{2-}$ ($n \geq 6$) which are presently being investigated.⁴ Infrared solution

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

(2) S. Martinengo and P. Chini, *Gazz. Chim. Ital.*, **102**, 344 (1972), and references therein.

(3) (a) G. Booth and J. Chatt, *J. Chem. Soc. A*, 2131 (1969), and references therein; (b) G. Booth, J. Chatt, and P. Chini, *Chem. Commun.*, 639 (1965).

(4) With Na-K alloy as a reducing agent one obtains a more reduced species which, because of its increased reactivity, has not yet been isolated in the solid state. Its infrared carbonyl frequencies of 1950 (vs) and 1745 (s) cm^{-1} in THF solution correspond to that expected for the $[Pt_3(CO)_3(\mu_2-CO)_3]^{2-}$ monomer.

spectra (Table I) show an expected lowering of corresponding terminal and bridging carbonyl frequencies upon successive reduction of dianions II through V.

Table I. Infrared Absorptions in the Carbonyl Stretching Region of the $[Pt_3(CO)_3(\mu_2-CO)_3]_n^{2-}$ Dianions

$[Pt_3(CO)_3(\mu_2-CO)_3]_n^{2-}$ anion	Color	ν_{CO} (cm^{-1} , THF solution)
II, $n = 5$	Yellow-green	2055 (vs), 1890 (w), 1870 (s), 1840 (w), 1825 (w)
III, $n = 4$	Blue-green	2045 (vs), 2025 (sh), 1880 (w), 1860 (s), 1840 (sh), 1828 (w)
IV, $n = 3$	Red-violet	2030 (vs), 1855 (sh), 1842 (s), 1835 (sh), 1810 (w)
V, $n = 2$	Orange-red	1990 (vs), 1818 (m), 1795 (s)

X-Ray structural investigations of these diamagnetic dianions⁵ have been carried out^{6,7} for II, IV, and V and are currently underway⁶ for III.⁸ The structures (Figure 1) of the $[Pt_3(CO)_3(\mu_2-CO)_3]_2^{2-}$ dianion (V), the $[Pt_3(CO)_3(\mu_2-CO)_3]_3^{2-}$ dianion (IV), and the $[Pt_3(CO)_3(\mu_2-CO)_3]_5^{2-}$ dianion (II) are all based upon the polymerization of a common triplatinum hexacarbonyl component by further direct Pt-Pt bonding.

The geometry of the hexaplutonium dianion (V), which has crystallographic C_2 -2 site symmetry, ideally conforms to D_{3h} - $62m$ hexagonal symmetry with the six platinum atoms arranged in a trigonal-prismatic array. Figure 1 shows a small but significant translational distortion of the two symmetry related $Pt_3(CO)_3(\mu_2-CO)_3$ fragments from an eclipsed D_{3h} conformation by *ca.* 0.51 Å along one of the triangular Pt-Pt edges. Also observed is a detectable tilting in each triplatinum moiety of both the terminal and bridging carbonyls in an outward direction from their triplatinum plane. A comparison of its *trigonal-prismatic* metal framework which is in contradistinction with the *trigonal-antiprismatic* (or octahedral-like) metal array in the congener

(5) We are indebted to Mr. James Kleppinger at the University of Wisconsin (Madison) who carried out magnetic susceptibility measurements *via* the Faraday method.

(6) (a) $[Pt(C_6H_5)_3]_2[Pt_3(CO)_3(\mu_2-CO)_3]_2$ (V): monoclinic, $C2/c$; $a = 18.882$ (4), $b = 14.677$ (3), $c = 22.860$ (7) Å, $\beta = 110.67$ (2)°, $V = 5927$ (2) Å³; $\rho_{obsd} = 2.47$ vs. $\rho_{calcd} = 2.45$ g cm^{-3} for $Z = 4$. Anisotropic least-squares refinement gave $R_1(F) = 5.6\%$ and $R_2(F) = 5.9\%$ for 1506 independent diffractometry data ($I > 2\sigma(I)$). (b) $[Pt(C_6H_5)_3]_3[Pt_3(CO)_3(\mu_2-CO)_3]_3$: monoclinic, $C2/c$; $a = 20.123$ (3), $b = 14.311$ (3), $c = 26.433$ (5) Å, $\beta = 115.22$ (6)°, $V = 6886$ (2) Å³; $\rho_{obsd} = 2.83$ vs. $\rho_{calcd} = 2.83$ g cm^{-3} for $Z = 4$. Anisotropic least-squares refinement gave $R_1(F) = 6.3\%$ and $R_2 = 6.8\%$ for 2436 independent diffractometry data ($I > 2\sigma(I)$). (c) $[As(C_6H_5)_3]_3[Pt_3(CO)_3(\mu_2-CO)_3]_3$: triclinic, $P\bar{1}$; $a = 15.239$ (5), $b = 19.377$ (14), $c = 14.628$ (5) Å, $\alpha = 106.66$ (4), $\beta = 101.10$ (3), $\gamma = 85.65$ (5)°; $V = 4059$ (3) Å³; the structural determination in progress involves the use of 5322 independent diffractometry data ($I > 2\sigma(I)$). (d) $[As(C_6H_5)_3]_2[Pt_3(CO)_3(\mu_2-CO)_3]_2$ (II): triclinic, $P\bar{1}$; $a = 14.783$ (8), $b = 26.426$ (13), $c = 13.835$ (4) Å, $\alpha = 102.73$ (3), $\beta = 118.16$ (3), $\gamma = 95.28$ (4)°; $V = 4524$ (3) Å³; $\rho_{obsd} = 3.33$ vs. $\rho_{calcd} = 3.33$ g cm^{-3} for $Z = 2$. Anisotropic least-squares refinement gave $R_1(F) = 5.9\%$ and $R_2(F) = 6.3\%$ for 3558 independent diffractometry data ($I > 2\sigma(I)$).

(7) For computation of distances and bond angles, see paragraph at end of paper regarding supplementary material.

(8) All crystallographic programs (except that for absorption corrections) utilized in the structural determinations and least-squares refinements were written by one of us (J. C. C.).

nickel analog, $[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$, is given elsewhere.^{9,10}

The nonaplatinum dianion IV of crystallographic site symmetry C_2 -2 also may be considered to possess an idealized D_{3h} geometry consisting of two trigonal-prismatic $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2$ fragments fused to each other on one common triangular face. Figure 1 reveals that the resulting three triangular platinum fragments are considerably distorted from a regular eclipsed D_{3h} conformation primarily by a helical twisting of each fragment relative to its adjacent one(s) by *ca.* 13° about the pseudotrifold axis.

The pentadecaplatinum dianion II, which has no required crystallographic symmetry constraints, may be envisioned as being formed from the fusion on a triangular platinum face of two doubly prismatic $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]$ fragments. Figure 1 clearly shows that whereas the bottom of the five $\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3$ layers is virtually eclipsed (*i.e.*, within 0.2°) with respect to the next layer, the top layer is twisted by *ca.* 8.1° from its neighbor; moreover, the central layer is almost equivalently twisted by *ca.* 27.2 and 28.6° relative to its two adjacent inner ones.

The following stereochemical results and conclusions are offered on the basis of a comparison of the prominent structural features. (1) The observed distortions from a regular prismatic stacking of platinum atoms represent a compromise between steric effects (imposed by nonbonding repulsions mainly between the carbonyl ligands of adjacent layers) and electronic effects which appear to favor a regular trigonal-eclipsed metal geometry. The observed types of geometrical distortions (which result in increased separations between carbonyl ligands) include a composite of translational shifts and twisting deformations of the neighboring $\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3$ layers with tilting of the carbonyl ligands away from the adjacent layers being possible only for the two outermost layers.¹¹ (2) The individual *intratriangular* Pt-Pt distances in V, IV, and II are all within 0.01 Å of the identical average value of 2.66 Å for the three dianions. This value, which is within the expected range for Pt-Pt single bonds,¹² compares favorably to the average value of 2.65 Å found¹³ in the phosphine-substituted *neutral* monomeric analog, $\text{Pt}_3(\text{PR}_2\text{R}')_3(\mu_2\text{-CO})_3$ (where R = C₆H₅, R' = CH₂C₆H₅) but is significantly shorter than the average values of 2.75 and 2.79 Å determined¹⁴ for the two types of carbonyl-bridged Pt-Pt bonds in $\text{Pt}_4(\text{PR}_2\text{R}')_4(\mu_2\text{-CO})_5$

(9) The only other example of a trigonal prismatic cluster of metal atoms is the $[\text{Rh}_6(\text{CO})_8(\mu_2\text{-CO})_6\text{C}]^{2-}$ dianion of D_{3h} geometry which has a carbide atom at the center of the prism with all nine edges spanned by symmetrically bridging carbonyl ligands: V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 651 (1973).

(10) J. C. Calabrese, A. Cavalieri, P. Chini, L. F. Dahl, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, **96**, 2516 (1974).

(11) In the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$ dianion (II) the angular distortions of the inner three layers relative to one another are close to 30° which represents an intermediate conformation between an eclipsed and staggered interaction thereby allowing a minimum steric interaction among carbonyl ligands of adjacent layers. In the case of the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_3^{2-}$ dianion (IV) where the carbonyl ligands of the outer two triangles can tilt away from those of the central triangle, the rotation of the adjacent layers about the quasi-threefold axis is decreased to approximately one-half of 30°.

(12) (a) A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. A*, 2772 (1969); (b) K. K. Cheung, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *Chem. Commun.*, 875 (1971).

(13) P. M. Cook, L. F. Dahl, P. Chini, and J. Chatt, *in press*.

(14) R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Amer. Chem. Soc.*, **91**, 1574 (1969).

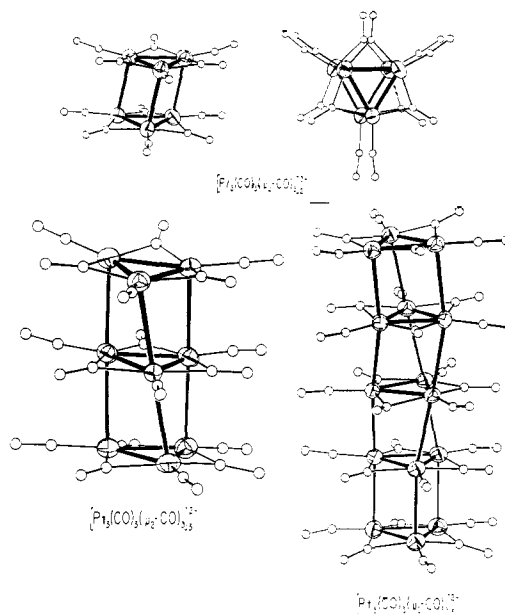


Figure 1. Structures of the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$ dianion (V), the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_3^{2-}$ dianion (IV), and the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_5^{2-}$ dianion (II).

(where R = CH₃, R' = C₆H₅). (3) The *intertriangular* Pt-Pt distances in the three dianions exhibit wider individual ranges and slightly different average values, *viz.*, 3.03–3.05 and 3.04 Å (av) in V, 3.04–3.06 and 3.05 Å (av) in IV, and 3.05–3.10 and 3.08 Å (av) in II. The parallel nature of the triplatinum layers in these dianions is illustrated by the angles between adjacent triplatinum planes being 0.4° in V, 1.8° in IV, and 0.6–0.8° range in II. The essentially equivalent *intertriangular* Pt-Pt distances are made compatible with the considerable variations in twisting deformations (and translational distortion for V) between adjacent layers through an appropriate counterbalancing in the perpendicular distances between the adjacent triplatinum layers. (4) Although a considerable variation in individual Pt-CO distances is observed, nevertheless, similar average values are found for the three dianions which distinctly show that the Pt-CO(bridging) bond lengths are *ca.* 0.2 Å longer than the Pt-CO(terminal) ones, *viz.*, 2.03 *vs.* 1.77 Å for V, 2.00 *vs.* 1.79 Å for IV, and 2.03 *vs.* 1.80 Å for II. (5) In light of the existence of these dianions, it seems highly probable that the so-called $[\text{Pt}(\text{CO})_2]_n$ polymer³ may indeed be correspondingly formulated as a long-chain $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_n^{2-}$ derivative with presumably hydronium counterions. (6) This observed repetition of a fundamental $\text{M}_3\text{L}_3(\mu_2\text{-X})_3$ structural unit and the constancy of the anionic charge make it necessary to invoke a molecular orbital model, analogous to the qualitative one utilized¹⁵ for the $[\text{M}_2\text{Ni}_3(\text{CO})_{13}(\mu_2\text{-CO})_3]^{2-}$ dianions (where M = Cr, Mo, W), in order to delocalize the negative charge over the entire platinum cluster system in each platinum dianion.

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(15) J. K. Ruff, R. P. White, Jr., and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 2159 (1971).

Center, University of Wisconsin (Madison), was made available through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee.

Supplementary Material Available. A listing of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-2614.

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Synthesis and Structure of a Hexanuclear Nickel Carbonyl Dianion, $[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$, and Comparison with the $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$ Dianion. An Unprecedented Case of a Metal Cluster System Possessing Different Metal Architectures for Congener Transition Metals¹

Sir:

We wish to report the isolation and structural characterization of the $[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$ dianion which represents the first unambiguous example of a hexanuclear metal carbonyl cluster system with 12 ligands. Of prime importance to the field of metal carbonyl chemistry is that this research combined with the subsequent preparation and structural analysis² of the hexaplatinum carbonyl analog, $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$, has established for the first time that direct metal-metal interactions involving a first-row transition metal can be sufficiently different from those involving a congener third-row transition metal such as to give rise to two different metal frameworks which are conformers of each other.^{3,4}

Prior to this work, the syntheses of various nickel carbonyl anions formulated as $[\text{Ni}_2(\text{CO})_6]^{2-}$, $[\text{Ni}_3(\text{CO})_6]^{2-}$, $[\text{Ni}_4(\text{CO})_9]^{2-}$, and $[\text{Ni}_5(\text{CO})_9]^{2-}$ have been reported⁵ in the literature. Since the stoichiometries of these unusual polymeric species cannot be unequivocally characterized by the usual chemical and physical methods, a reinvestigation of the nickel carbonyl anions has been initiated involving X-ray diffraction studies to ascertain their formulas as well as to obtain definitive

information concerning the structural interrelationships and bonding of the complexes.

The $[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$ dianion was prepared by reduction of nickel tetracarbonyl. The reduction reaction is extremely dependent on the reducing agent used and upon the experimental conditions with infrared solution spectra providing evidence for at least six different anionic species, of which one of intense red color predominates on account of its relative ease of formation and stability to hydrolysis. For example, this anion can be prepared through the reduction of $\text{Ni}(\text{CO})_4$ either with sodium metal in THF (60°, 20 hr) or with potassium hydroxide in methanol (55°, 5 hr). Evaporation of solvent followed by redissolution in water and saturation with solid potassium bromide yields the potassium salt in a crystalline dark red form (ca. 25–60% yield). The corresponding tetramethylammonium salt, obtained from metathesis of the potassium salt in water and recrystallized from acetone-isopropyl alcohol, is diamagnetic⁶ and moderately stable in air. An infrared spectrum of the sodium salt in THF solution reveals carbonyl absorption bands at 1975 (s), 1810 (m), 1790 (m), and 1743 (w) cm^{-1} ; the reasonable agreement of these values with those previously reported⁷ for the sodium salt of the presumed $[\text{Ni}_3(\text{CO})_6]^{2-}$ anion (*viz.*, 1985 (s), 1818 (ms), and 1799 (ms) cm^{-1} in THF solution) offers convincing evidence that the two anions may in fact be identical. Since our elemental analyses instead suggested an empirical formula of $[\text{Ni}_3(\text{CO})_6]_n^{n-}$, its actual composition as a $[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$ dianion was ascertained from an X-ray diffraction analysis of the tetramethylammonium salt.^{8,9}

This dianion of crystallographic $C_{3i}\bar{3}$ site symmetry has an idealized $D_{3d}\bar{3}2/m$ geometry (Figure 1) which may be envisioned as a trigonal-antiprismatic array of metal atoms formed from the dimerization of two planar $\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3$ moieties through direct Ni-Ni interactions involving the two additional anionic electrons.

The symmetry-related Ni-Ni bonds within both $\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3$ triangles are 2.38 Å in length, while the other six equivalent Ni-Ni bonds between them are 2.77 Å. This elongated distortion of the octahedron of nickel atoms along the crystallographic threefold axis thereby results in two smaller transoid, equilateral triangular metal faces, whose edges are symmetrically bridged by carbonyls, and six isosceles triangular faces with two longer edges. The two independent Ni-CO(bridging) bond lengths are both 1.90 Å which is 0.25 Å longer than the one independent Ni-CO(terminal) bond length of 1.75 Å; the bridging and terminal C-O distances are 1.17 and 1.13 Å, respectively.

The transformation from a trigonal-antiprismatic (or octahedral-like) metal arrangement in $[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$ dianion to a trigonal-prismatic one in the cor-

(1) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

(2) J. C. Calabrese, P. Chini, L. F. Dahl, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, **96**, 2614 (1974).

(3) Previously determined structural dissimilarities between polynuclear metal carbonyl complexes (of the same general formula) for first-row transition metals compared to those for third-row transition metals have involved different arrangements of carbonyl ligands, *e.g.*, $\text{Fe}_3(\text{CO})_{10}(\mu_2\text{-CO})_2$ vs. $\text{Os}_3(\text{CO})_{12}$ and $\text{Co}_3(\text{CO})_9(\mu_2\text{-CO})_3$ vs. $\text{Ir}_3(\text{CO})_{12}$.

(4) P. Chini, *Inorg. Chim. Acta Rev.*, **2**, 31 (1968).

(5) Cf. F. Calderazzo, R. Ercoli, and G. Natta in "Organic Synthesis Via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, pp 68–70, and references cited therein.

(6) We are indebted to Mr. James Kleppinger at the University of Wisconsin (Madison) for making the magnetic susceptibility measurements *via* the Faraday method.

(7) W. Hieber and J. Ellermann, *Z. Naturforsch. B*, **18**, 595 (1963).

(8) $[\text{N}(\text{CH}_3)_4]_2[\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2$: trigonal, $P\bar{3}$; $a = b = 11.003$ (1), $c = 7.045$ (1) Å; $V = 738.7$ Å³; $\rho_{\text{caled}} = 1.88$ g cm^{-3} for $Z = 1$. Anisotropic least-squares refinement gave $R_1(F) = 3.9\%$ and $R_2(F) = 4.0\%$ for 614 independent diffractometry data ($I > 2\sigma(I)$).

(9) For computation of distances and bond angles, see paragraph at end of paper regarding supplementary material.