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 (21) There is a preliminary account of an authentic discrete C_{4v} structure for the Sn_9^{4-} metal cluster in $[Na(2,2,2-crypt)^+]_4Sn_9^{4-}$: J. D. Corbett and P. A. Edwards, *J. Chem. Soc., Chem. Commun.*, 984 (1975). The dihedral angles between planes perpendicular to the fourfold axis are about 3° (J. D. Corbett, private communication). Electronic features, orbital energy separations, and possible degeneracies may dictate whether a D_{3h} or C_{4v} type of polyhedron is adopted in clusters.
 (22) In triangular polyhedral faces for cluster complexes, the observed and theoretically expected situations are (a) equilateral triangular faces where vertex atoms have the same connectivity, (b) isosceles triangular face with AA edge longer where vertex A has a higher connectivity than vertex B, (c) an isosceles triangular face with AA edge shorter where vertex A has a lower connectivity than vertex B, and (d) vertex positions of highest connectivity are closer to the polyhedral center than vertex positions of lower connectivity.

Synthesis and Chemical Characterization of Platinum Carbonyl Dianions $[Pt_3(CO)_6]_n^{2-}$ ($n = \sim 10, 6, 5, 4, 3, 2, 1$). A New Series of Inorganic Oligomers

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Abstract: Reduction of $Na_2PtCl_6 \cdot 6H_2O$ or $Pt(CO)_2Cl_2$ under carbon monoxide (25 °C, 1 atm) in the presence of alkali gives the dianions $[Pt_3(CO)_6]_n^{2-}$ ($n = \sim 10, 5, 4, 3$) where n depends on the alkali:Pt ratio. Other members of this series ($n = 6, 2, 1$) have been obtained starting from preformed $[Pt_3(CO)_6]_n^{2-}$ ($n = 10, 5, 4, 3$) by reduction with lithium metal ($n = 2, 1$) and sodium-potassium alloy ($n = 1$) or by oxidation with Pt(IV) ($n = 6$). These last preparations and the redistribution of metal bonds between oligomers which differ in n by to or more ($n \leq 6, \Delta n \geq 2$) point out the ease with which these compounds change nuclearity. Increasing n decreases the reactivity towards electrophiles and oxidizing agents and, at the same time, the reactivity towards nucleophiles and reducing agents increases. The first example of a platinum carbonyl catalyzed hydroformylation reaction is reported. The main bonding features of these dianions, and the different stabilities of analogous nickel, palladium, and platinum carbonyl compounds, are discussed.

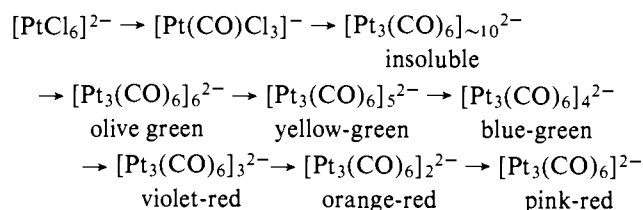
Our interest in the chemistry of the platinum(0) clusters containing tertiary phosphines and carbon monoxide as ligands²⁻⁴ prompted us to investigate the nature and the reactivity of the platinumdicarbonyl, $[Pt(CO)_2]_n$.⁵ This compound, which was first isolated by Booth and Chatt, has not been sufficiently characterized owing to its complete insolubility. The starting point of our research has been the observation that platinumdicarbonyl dissolves in acetone in the presence of aqueous ammonia to give dark green uncharacterized solutions.⁵

Although this work began in 1967,⁶ it has only been possible to obtain the platinum carbonyl derivatives on a preparative scale some years later when we used the reductive carbonylation of platinum(IV) salts in alkaline solution, which had been successfully used for the preparation of rhodium carbonyl clusters.⁷ Furthermore the structural characterization of the $[Pt_3(CO)_6]_n^{2-}$ derivatives has been hampered by difficulties such as loss of crystallinity due to elimination of clathrated solvents, or crystal disorder, although these problems have been overcome recently by using bulky cations.^{8,9}

Results and Discussion

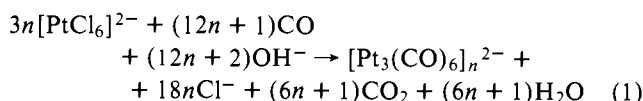
1. Synthesis of $[Pt_3(CO)_6]_n^{2-}$. The series of dianions with general formula $[Pt_3(CO)_6]_n^{2-}$ ($n = \sim 10, 6, 5, 4, 3, 2, 1$) has been synthesized from several platinum substrates ($Na_2PtCl_6 \cdot 6H_2O$, $H_2PtCl_6 \cdot xH_2O$, Na_2PtCl_4 , $Pt(CO)_2Cl_2$) using various reducing agents (alkali hydroxides under CO, $Fe(CO)_5$, cobaltocene, alkali metals). Although the value of n of the final product depends greatly on the nature of the reagents as well as on the experimental conditions, by carrying out the reaction at room temperature and under carbon mon-

oxide, the reductive carbonylation proceeds following the sequence:¹⁰



Beginning from $n = 6$, the salts of consecutive dianions ($\Delta n = 1$) have similar solubilities and their separation is always difficult and often impossible. It has therefore been necessary to find suitable experimental conditions in order to carry out selectively each step of the above sequence. The course of this reduction is conveniently monitored by infrared spectroscopy.

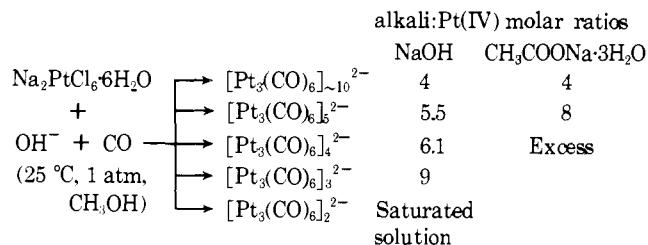
The most important synthetic method consists in the progressive reduction of platinum(IV) salts in the presence of alkali and carbon monoxide according to the following general stoichiometric equation:



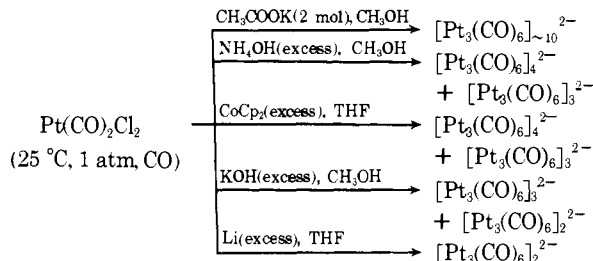
The best platinum starting material is the sodium hexachloroplatinate because it is readily available and fairly soluble in alcoholic solvents. The most reliable experimental conditions using this route are summarized in Scheme I.¹¹

The clear orange solution of sodium hexachloroplati-

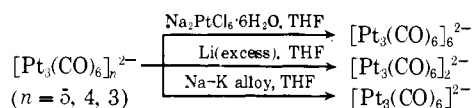
Scheme I



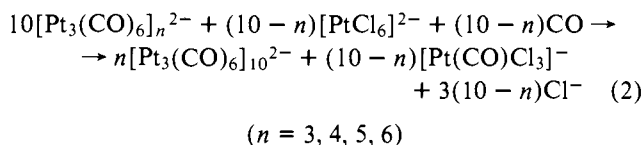
Scheme II



Scheme III



nate(IV) becomes yellow and cloudy upon addition of alkali and carbon monoxide. After an activation time of 3–4 h, the reductive carbonylation begins. Sometimes longer activation times are required but it is generally sufficient to warm the solution to 50 °C in order to speed up the process. Once started the reduction is fast owing to an autocatalytic effect such as that represented in eq 2:



Sodium acetate is particularly useful for the selective synthesis of [Pt₃(CO)₆]₅²⁻, because further reduction only occurs with considerable excess of this reagent (see Scheme I). Similarly, further reduction of [Pt₃(CO)₆]₃²⁻ only occurs with an excess of sodium hydroxide. In both cases, this reduces the necessity for strict control of the alkali:Pt ratio.

The alkali:Pt ratios reported in Scheme I refer to reactions in methanol solution. In other solvents, such as dimethyl sulfoxide or dimethylformamide, in which the nucleophilic power of hydroxides is enhanced, selective reduction is not easily obtained.

Similar results have been obtained using Pt(CO)₂Cl₂ (Scheme II); however, because this route employs less accessible starting materials, no particular effort has been made to optimize the selective conditions.

The dianions [Pt₃(CO)₆]_n²⁻ (n = 6, 2, 1), which are not easily or directly prepared from the reductive carbonylation of Na₂PtCl₆·6H₂O, are most conveniently prepared as shown in Scheme III.

The first reaction in Scheme III corresponds (for n = 4) to the following stoichiometry:

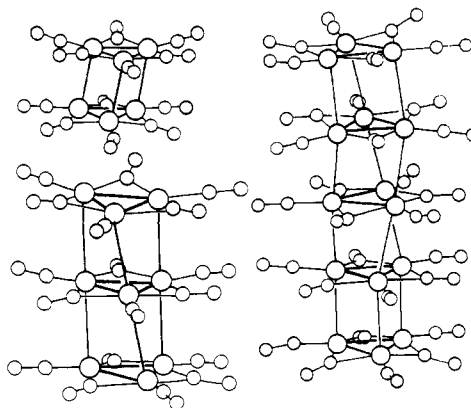
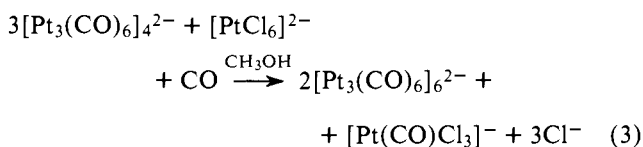


Figure 1. Structures of [Pt₃(CO)₆]_n²⁻ (n = 5, 3, 2).

Consistent with this stoichiometry, infrared spectra show this reaction to be complete after addition of ca. 0.35 mol of sodium hexachloroplatinate(IV) per mole of [NBu₄]₂[Pt₃(CO)₆]₄. A slight excess of oxidizing agent does not depress the yield; although, particularly in methanol, a greater excess results in precipitation of [Pt₃(CO)₆]_{~10}²⁻.

The [Pt₃(CO)₆]_{~10}²⁻ dianion can be also prepared by reduction of sodium hexachloroplatinate(IV) or H₂PtCl₆·xH₂O with excess Fe(CO)₅ in methanol solution.

2. Analytical and Spectroscopic Data. The insoluble product which for brevity we have formulated as [Pt₃(CO)₆]_{~10}²⁻ could be a pure single derivative but much more likely is probably a mixture of different oligomers with an average nuclearity of 30. In fact, its appearance and analytical data change on changing the experimental conditions. For instance the silky precipitate obtained by reductive carbonylation of sodium hexachloroplatinate(IV) in the presence of sodium acetate has been shown by atomic absorption analysis to contain ca. 15:1 Pt:Na⁺ ratio, and the silky precipitate obtained by reduction of Na₂PtCl₆·6H₂O or H₂PtCl₆·xH₂O with Fe(CO)₅ has a ca. 30:1 Pt:Fe²⁺ ratio.¹² On the contrary the products isolated by slow carbonylation of [NBu₄]₂[PtCl₆] as well as by slow oxidation of [NBu₄]₂[Pt₃(CO)₆]₄ with sodium hexachloroplatinate(IV) have on the average a lower nuclearity (Pt:NBu₄ ca. 12:1). These last products, and above all the corresponding tetraheptylammonium derivative, while are still insoluble in methanol or THF, show a slight solubility in acetone and acetonitrile where they give pale green solutions whose ir are practically coincident with that of the [Pt₃(CO)₆]₆²⁻ dianion (see later).

The formulation of the [Pt₃(CO)₆]₆²⁻ dianion has been established by analysis of the crystalline tetraphenylphosphonium salt (Pt:PPh₄ = 8.6:1). The empirical formulas for the analogous dianions (n = 5, 4, 3, 2) have been established similarly, and have since been confirmed by x-ray structural determinations.^{8,9} The structures of [Pt₃(CO)₆]_n²⁻ (n = 5, 3, 2) are schematically represented in Figure 1 and show that these oligomers result from the stacking of Pt₃(CO)₃(μ₂-CO)₃ triangular units along the pseudo-threefold axis. These oligomers become increasing soluble in organic solvents with decreasing values of n.

The formulation of [Pt₃(CO)₆]₂²⁻, which could not be isolated in a pure crystalline state owing to its lability, is based on the analysis of the clear pink-red THF solution obtained by reduction of Na₂[Pt₃(CO)₆]_{~10} with Na-K alloy immediately after the ir spectrum had shown that the trinuclear dianion was the only carbonyl species present in solution (Pt:Na + K = 1.58:1).

The carbonyl stretching region of the infrared spectra of these oligomers is reported in Figure 2. In agreement with the presence of a Pt₃(CO)₃(μ₂-CO)₃ triangular unit periodically repeated along the ternary axis, the infrared spectra of all these

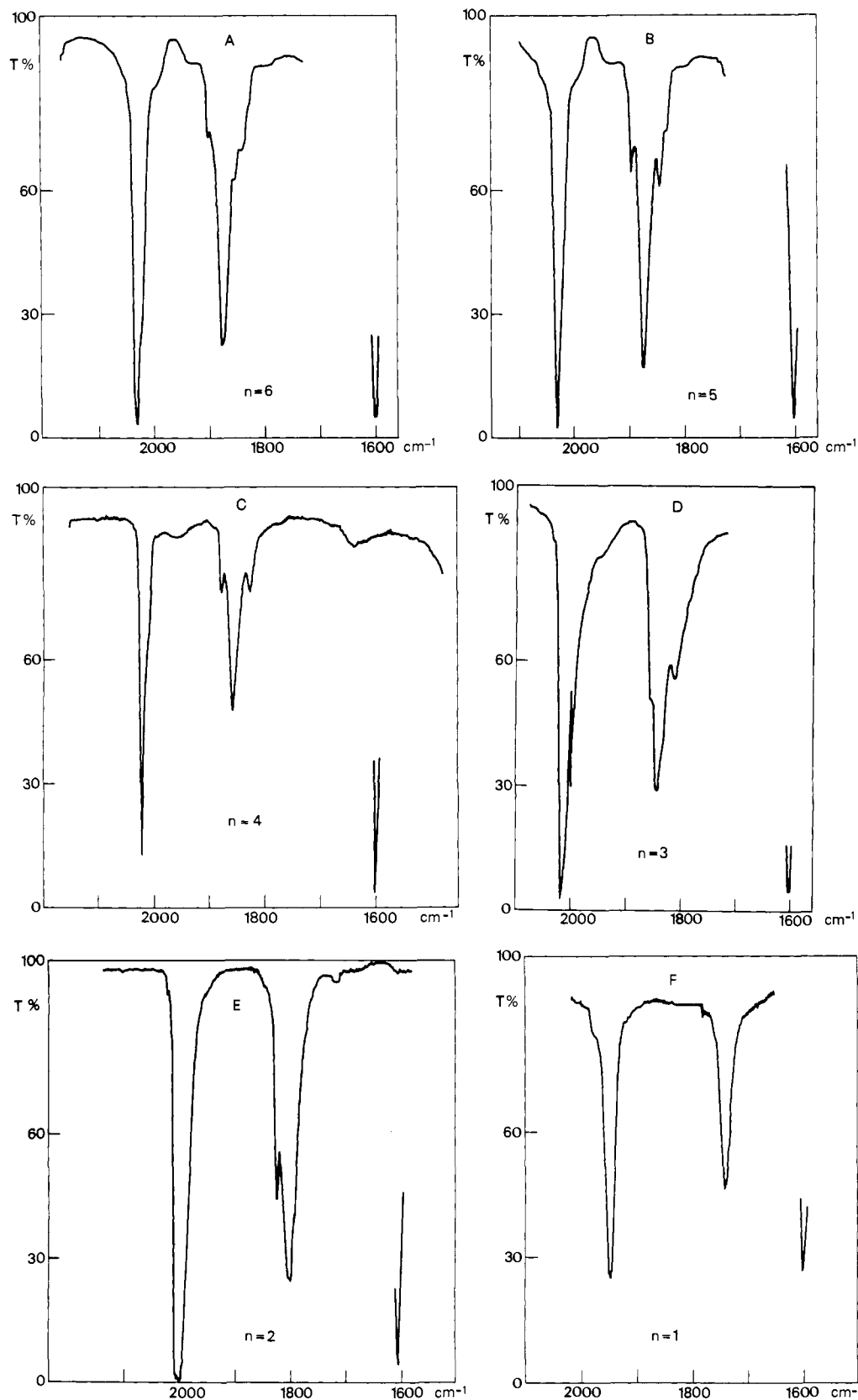


Figure 2. Infrared spectra of the $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianions in THF solution: A ($n = 6$) 2065 vs, 1900 sh, 1875 s, 1855 sh, 1840 sh cm^{-1} ; B ($n = 5$) 2055 vs, 1890 mw, 1870 s, 1840 mw, 1830 sh cm^{-1} ; C ($n = 4$) 2040 vs, 2030 sh, 1880 mw, 1860 s, 1825 mw cm^{-1} ; D ($n = 3$) 2030 vs, 1855 sh, 1840 s, 1830 sh, 1810 m cm^{-1} ; E ($n = 2$) 1995 vs, 1818 m, 1795 s cm^{-1} ; F ($n = 1$) 1945 vs, 1740 s cm^{-1} .

dianions show an almost identical pattern. The absorption frequencies are of the same order of magnitude of those found in other carbonyl clusters with similar ratios between number of metal atoms and negative charges; compare for instance the values for ν_{CO} terminal in $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$

(2045 and 2053–2040 cm^{-1} , respectively) and in $[\text{Pt}_3(\text{CO})_6]_2^{2-}$ and $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ (1990 and 1980 cm^{-1} , respectively).^{14,15} A decrease in the number of metal atoms per negative charge results in a shift of ν_{CO} to lower frequencies (Figure 3). The presence of a nonlinear relationship suggests

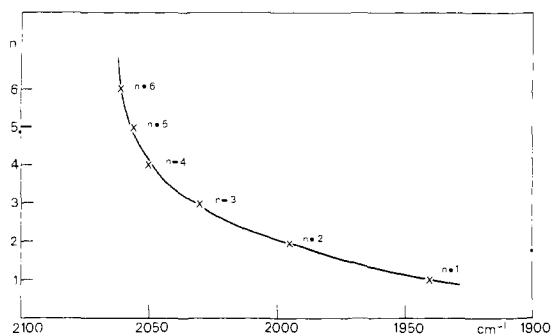
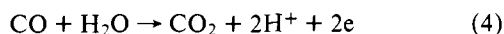


Figure 3. Relationship between number of metal atoms per negative charge and absorption frequencies of the terminal CO groups.

some competition between the carbonyl groups and the metal skeleton in delocalizing the negative charge. Furthermore Figures 2 and 3 show that for $n > 6$ the $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianions should have infrared spectra practically coincident with $[\text{Pt}_3(\text{CO})_6]_6^{2-}$, as found for the tetrabutyl- and tetraheptylammonium salts of $[\text{Pt}_3(\text{CO})_6]_{\sim 10}^{2-}$. This observation is significant with respect to the formulation of platinumdicarbonyl which has an ir spectrum (Nujol mull) practically coincident with that of the $[\text{Pt}_3(\text{CO})_6]_{\sim 10}^{2-}$ dianion. Platinum dicarbonyl presents also chemical behavior quite similar to that of $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n > 6$) and therefore it is probably an anionic derivative with n greater than 6 and possibly close to 10. Such a conclusion implies that the hydronium ion, H_3O^+ , is the cationic counterpart when this compound is obtained by simple hydrolysis of $\text{Pt}(\text{CO})_2\text{Cl}_2$ in wet diethyl ether or benzene. Recent reports show that similar hydronium salts of $[\text{Rh}_6(\text{CO})_{15}(\text{COOR})^-]$ ($\text{R} = \text{Et}, \text{Pr}$),¹⁶ $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$,¹⁶ and $[\text{Rh}_{15}(\text{CO})_{28}(\text{C}_2)]^{-17}$ are quite stable.

3. Chemical Behavior. As already pointed out the reactivity of $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ depends on the value of n , and generally the trend is that increasing n results in an increase in reactivity towards nucleophilic and reducing agents, while decreasing n results in an increase in reactivity towards electrophiles and oxidizing agents.

For instance, we have already seen in the preceding section that the reactivity towards alkali under carbon monoxide decreases on decreasing n , so that the most reduced species ($n = 2, 1$) are best synthesized by reduction with alkali metals. In this context it is worth mentioning that, at the beginning of the series ($n = \sim 10$), water itself under carbon monoxide behaves like a nucleophile. Thus $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{\sim 10}$ suspended in wet THF under carbon monoxide atmosphere slowly dissolves giving a green solution due to its reduction to a mixture of $[\text{Pt}_3(\text{CO})_6]_6^{2-}$ and $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ dianions. This reaction results in an increase in acidity of the solution (eq 4):

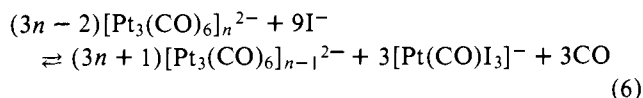


and the final composition is probably a compromise between reduction due to water and reverse oxidation (eq 5) due to the corresponding set-free acidity (see also later):



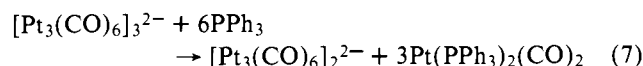
Addition of excess strong acids to $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 5, 4, 3, 2$) results always in a formal oxidation and formation of $[\text{Pt}_3(\text{CO})_6]_{\sim 10}^{2-}$. The reactivity towards acid increases on decreasing n to the point that the $[\text{Pt}_3(\text{CO})_6]_2^{2-}$ dianion is sensitive even to humidity. Water then displays an opposite effect towards dianions which are at the extremes of the series: reduction when $n = \sim 10$, and oxidation when $n = 1$.

Reactions with other nucleophiles such as iodide and triphenylphosphine result in reduction by disproportionation. In the first case, the reaction is represented by the general equation (6)



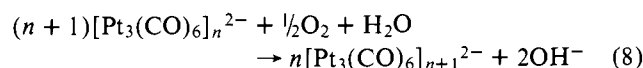
and involves the disproportionation of the cluster to a more reduced oligomer and to a Pt(II) species. This disproportionation has been proved for $n = \sim 10, 6, 5, 4, 3$ and under carbon monoxide it has been found to be an equilibrium which is dependent on the solvent and the concentration of the reagents.

With triphenylphosphine the disproportionation occurs with formation of Pt(0) species according to eq 7:



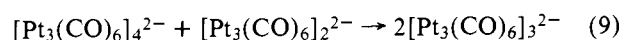
However, the stoichiometry of this reaction is further complicated by the equilibrium between $\text{Pt}(\text{PPh}_3)_2(\text{CO})_2$ and $\text{Pt}(\text{PPh}_3)_3(\text{CO})$.¹⁸

The reactivity towards oxidizing agents increases on decreasing n and the dianions ($n = 3, 2, 1$) are very sensitive to atmospheric oxygen with which they react according to the following general equation:

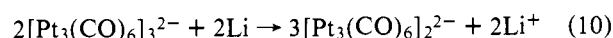


The reaction system is once again rather complicated, and the formation of hydroxide ions, according to eq 8, seems to be responsible for the reverse reductive carbonylation; thus green solutions of $[\text{Pt}_3(\text{CO})_6]_4^{2-}$, obtained by oxidation of $[\text{Pt}_3(\text{CO})_6]_3^{2-}$, turn red for partial back-reduction to $[\text{Pt}_3(\text{CO})_6]_3^{2-}$ once under inert atmosphere. The reaction with oxygen becomes much slower when $n \geq 4$ and a fast oxidation requires stronger oxidizing agents such as iodine or Pt(IV) salts.

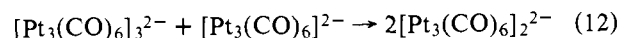
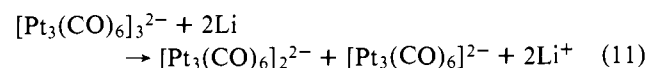
A peculiarity of these oligomers is ready redox reaction between nonconsecutive oligomers ($n \leq 6, \Delta n \geq 2$) (eq 9):



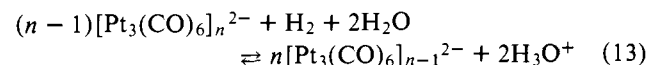
Such a redox reaction, which results in redistribution of metal bonds, allows a simple interpretation of the mechanism of the reduction reactions with alkali metals. For instance, the reduction reaction (10):



can be seen as a combination of the two reactions (11 and 12):



Another interesting observation is that $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianions, when $n > 3$, are reduced even by hydrogen (25 °C, 1 atm) according to the following equation (13):



The reaction is favorably affected by the presence of traces of water, which probably act by solvating the protons, and has been found to be an equilibrium reaction since substitution of the hydrogen by a nitrogen atmosphere results in the slow regeneration of the starting materials. When $n = 4$, aerial oxidation results in the reversal of reaction 13 through reaction 8, and by carrying out alternately the two reactions it has been possible to obtain stepwise formation of water from oxygen and hydrogen.

Although reaction 13 probably involves hydride interme-

diates their detection, by ^1H NMR, has so far been unsuccessful. However, intermediate formation of hydride species is in agreement with the fact that under pressure of hydrogen and carbon monoxide in the presence of olefins such as propylene and 1-pentene, hydroformylation reactions have been observed. In particular, at 120 °C and under a pressure of 100 atm of hydrogen and carbon monoxide, 1-pentene is catalytically converted in the presence of $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ to an almost equimolar mixture of normal and isoaldehydes. At the end of the reaction, the platinum is recovered as a mixture of $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ and $[\text{Pt}_3(\text{CO})_6]_3^{2-}$. Traces of aldehydes, instead of the corresponding acids, have also been detected on reacting $[\text{Pt}_3(\text{CO})_6]_{\sim 10}^{2-}$ with water under CO (100 atm, 150 °C).

Hydroformylation catalyzed by platinum substrates has been reported in a number of patents,^{19–21} but this appears to be an unambiguous example of hydroformylation with unsubstituted platinum carbonyl catalysts.²²

Although a systematic investigation of the thermal stabilities is still in progress, the decomposition temperatures of $[\text{NBu}_4]_2[\text{Pt}_3(\text{CO})_6]_n$ ($n = 6, 5, 4$) are in the range 120–150 °C and the thermogravimetric measurements show that the decompositions take place with intermediate formation of other carbonyl derivatives currently under investigation.

4. Bonding Requirements of the $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ Dianions.

Platinum, in a low oxidation state, shows a great tendency to give clusters based on triangular units which have electronic configurations involving either 42 valence electrons as in $\text{Pt}_3(\text{PPh}_2\text{CH}_2\text{Ph})_3(\mu_2\text{-CO})_3$ ³ and $\text{Pt}_3(\text{CN-}t\text{-Bu})_3(\mu_2\text{-CN-}t\text{-Bu})_3$,²⁴ or 44 valence electrons as in $\text{Pt}_3(\text{PPh}_3)_4(\mu_2\text{-CO})_3$ ⁴ and $\text{Pt}_3(\text{COD})_3(\mu_3\text{-SnCl}_3)_2$.²⁵

The $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianion belongs to this second class of compounds, while the other $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n > 1$) dianions are a compromise between the two, since they can be considered formally to be derived from the condensation of a 44-valence electron $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]^{2-}$ unit with $n - 1$ $\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3$ units having 42 valence electrons. On this basis it therefore seems reasonable to conclude that a platinum trinuclear species having a 42-valence electron configuration is essentially stabilized through steric hindrance, otherwise the cluster tends to reach a more favorable 44-valence electron configuration by adding an extra ligand as in $\text{Pt}_3(\text{PPh}_3)_4(\mu_2\text{-CO})_3$ or by co-oligomerization as in $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_n^{2-}$.

A related 44-valence electron configuration has been recently discussed by Ruff, White, and Dahl for the $\text{Ni}_3(\text{CO})_3(\mu_2\text{-CO})_3$ triangular unit present in the $[\text{M}_2\text{Ni}_3(\text{CO})_6]^{2-}$ ($\text{M} = \text{Cr, Mo, W}$) dianions,²⁶ and the same bonding description can be used to explain the electronic configuration of the $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianions.

According to these authors, 18 electrons are allocated to nickel carbonyl σ bonding orbitals derived primarily from the valence 4s, 4p_x, and 4p_z atomic orbitals of each nickel atom. Another 18 electrons are allocated to the three in-plane bonding orbitals ($d_{z^2}(a'_1)^2$ and $d_{xz}(e')^4$) and to both the bonding and antibonding out-of-plane $d_{yz}(a''_2)^2$, $d_{xy}(e'')^4$, $d_{xy}(a''_1)^2$, and $d_{yz}(e'')^4$ orbitals. The remaining six 4p_y and 3d_{x²-y²} nickel valence orbitals set up a cyclopropenyl-like trinickel ring system which can interact with the σ -orbitals of the two axial $\text{M}(\text{CO})_5$ groups. The last 8 electrons can thus be allocated to two bonding and two nonbonding orbitals so that both the diamagnetism and the long Ni–M distances are rationalized.

By extending these ideas to $[\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3]_2^{2-}$, 72 out of the total 86 valence electrons could be employed for platinum–carbonyl σ bonding and intratriangular Pt–Pt interactions, while the remaining 14 electrons are available for Pt–Pt intertriangular bonds. Interaction of the cyclopropenyl-like triplatinum ring systems of the two $\text{Pt}_3(\text{CO})_3(\mu_2\text{-CO})_3$

moieties along the y axis should give rise to six weakly bonding and six weakly antibonding orbitals. The 14 electrons are assumed to fill both the bonding and antibonding combinations generated by the six valence d_{x²-y²} platinum orbitals and the a''₂ bonding combination of the p_y orbitals. Such an electronic configuration is in agreement with the diamagnetism of the molecule and, since just one electron pair is in a bonding situation between the two triangular units, it also accounts for the longer intertriangular Pt–Pt distances (3.04 Å in comparison to the intratriangular distances of 2.66 Å).⁸

In order to explain the constant Pt–Pt intratriangular distances on going from $n = 2$ to $n = 5$ and the diamagnetism of all these oligomers, the extension of this bonding scheme to dianions having n greater than 2 requires that just one electron pair is allotted in a bonding combination between each two adjacent triangular units, while the remaining $4n + 4$ electrons should mainly be in a nonbonding situation. This could be obtained by previous hybridization of the six cyclopropenyl-like triplatinum orbitals in two sets equivalent with respect to the triplatinum plane.

Finally we should mention that the number of valence electrons of these dianions ($42n + 2$) obeys Wade's rule for triangulated polyhedra.²⁷

5. Comparison between Carbonyl Compounds in the Ni–Pd–Pt Triad. The synthesis of the series of carbonylplatinate, $[\text{Pt}_3(\text{CO})_6]_n^{2-}$, and the structurally related carbonylnickelates, $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ ²⁸ and $[\text{Ni}_9(\text{CO})_{18}]^{2-}$,⁹ suggested the possibility of synthesizing the analogous palladium derivatives. However, reductive carbonylation of Na_2PdCl_4 and bis(benzonitrile)palladium dichloride both with alkali hydroxides under carbon monoxide and with $\text{Fe}(\text{CO})_5$, as well as reduction of preformed palladium carbonyl halides, always gave palladium metal even at low temperature. This raises the question why the stabilities of analogous carbonyl compounds of nickel, palladium, and platinum are so different.

A tetrahedral stereochemistry usually interpreted as involving a full use of the valence p orbitals is very common for nickel in a zero oxidation state (e.g., $\text{Ni}(\text{CO})_4$, $\text{NiL}_x(\text{CO})_{4-x}$, and $[\text{Ni}(\text{CO})_3\text{X}]^{2-}$),²⁹ while it is unstable in the binary carbonyls $\text{Pd}(\text{CO})_4$ ³⁰ and $\text{Pt}(\text{CO})_4$,³¹ although it can be stabilized by substitution of part of the carbonyl groups with less acidic ligands such as tertiary phosphines (e.g., $\text{PtL}_2(\text{CO})_2$).

Square-planar carbonyl halides, where a p orbital can be considered not to be involved in metal–ligand bonding, are common for platinum in +2 oxidation state (e.g. $\text{Pt}(\text{CO})_2\text{X}_2$, $[\text{Pt}(\text{CO})\text{X}_3]^-$, and $[\text{Pt}_2(\text{CO})_2\text{X}_4]^{2-}$),³² whereas the only well-characterized palladium analogues are $[\text{Pd}(\text{CO})\text{X}_3]^-$ and $[\text{Pd}_2(\text{CO})_2\text{X}_4]^{2-}$.³³ On the contrary square-planar nickel carbonyl halides have yet to be reported.

Partial use of such a p orbital corresponds, in the bonding picture we have given for the $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ dianions, to the formation of intertriangular metal bonds, and this possibility is verified also in the nickel case. The corresponding $\text{Pd}_3(\text{PPh}_3)_4(\text{CO})_3$ displays a reduced stability,³⁴ although it is possible that triangular units of type $\text{Pd}_3(\text{CO})_3\text{Cl}_3$ could be present in the not yet sufficiently characterized $[\text{Pd}(\text{CO})\text{Cl}]_n$ species.

Since the $(n - 1)d-np$ separation increases in the order $\text{Ni} < \text{Pt} < \text{Pd}$ (1.72, 3.28, and 4.23 eV mol⁻¹, respectively),³⁵ the isolation of the present compounds confirms the previous suggestion³⁵ that the $(n - 1)d-np$ separation is the most important variable responsible for the different stabilities of the analogous nickel, palladium, and platinum carbonyl compounds. A low separation energy should favor a tetrahedral zero oxidation state, an intermediate value should allow oligomers of the type $[\text{M}_3(\text{CO})_6]_n^{2-}$, and a high value could favor a square-planar (+2) oxidation state. However, a large value would correspond to insufficient back-donation (palladium case) and to a general low stability.

Experimental Section

All the reactions were carried out under nitrogen or carbon monoxide atmosphere in carefully purified solvents.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer using calcium fluoride cells. Na, K, Fe, and Pt metals were determined by atomic absorption using an AA-5 Varian Techtron spectrophotometer. Tetrasubstituted ammonium, phosphonium, and arsonium cations were determined as tetraphenylborates. Carbon monoxide has been determined as previously described.³⁶ $\text{Pt}(\text{CO})_2\text{Cl}_2$ was prepared according to the literature.³⁷

1. Synthesis of the $[\text{Pt}_3(\text{CO})_6]_{\sim 10}^{2-}$ Salts. (a) From $\text{Pt}(\text{CO})_2\text{Cl}_2$. $\text{Pt}(\text{CO})_2\text{Cl}_2$ (0.72 g, 2.23 mmol) was added under carbon monoxide to a cold (-70°C) solution of 0.49 g (4.99 mmol) of potassium acetate in methanol (20 ml). By 4 h stirring, while the temperature was raised to room temperature, a brown silky precipitate of $\text{K}_2[\text{Pt}_3(\text{CO})_6]_{\sim 10}$ was obtained. This was separated by filtration under nitrogen, washed with water and methanol, and dried under vacuum. Yield 0.5 g.

(b) From $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$. $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1.5 g, 2.67 mmol) was dissolved in a solution of 1.45 g (10.7 mmol) of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in methanol (25 ml). By 24 h stirring under carbon monoxide the solution separated out a brown silky precipitate of $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{\sim 10}$. This was filtered, washed with water and methanol, and dried under vacuum. Yield 0.62 g.

(c) From $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{CO})_5$. A solution of $\text{Fe}(\text{CO})_5$ (2.5 ml) in methanol (10 ml) was added drop by drop to a stirred solution of 3.03 g of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in methanol (50 ml) under carbon monoxide. A ready reaction took place with gas evolution and with formation of a brown-violet silky precipitate of $\text{Fe}[\text{Pt}_3(\text{CO})_6]_{\sim 10} \cdot x\text{MeOH}$ which was worked out as before. Yield 1.28 g. Similar results have also been obtained starting from $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$.

2. Synthesis of $[\text{PPh}_4][\text{Pt}_3(\text{CO})_6]_4$. A solution of 1.17 g (0.37 mmol) of $[\text{NMe}_4][\text{Pt}_3(\text{CO})_6]_4$ in methanol (30 ml) was treated drop by drop under carbon monoxide with a solution of 0.21 g (0.373 mmol) of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in methanol (15 ml). After addition of about 0.12 mmol of Pt(IV), the infrared spectrum of the reaction solution showed only absorptions due to the olive green dianion, $[\text{Pt}_3(\text{CO})_6]_6^{2-}$ (see Figure 2A). The green solution was filtered and solid tetraphenylphosphonium chloride was added. The resulting precipitate was filtered, washed with methanol, and dried under vacuum (yield 0.87 g). The compound was crystallized by dissolution in acetone (15 ml) and precipitation by slow diffusion of isopropyl alcohol (30 ml). In 2 days dark elongated prisms of $[\text{PPh}_4][\text{Pt}_3(\text{CO})_6]_6$ separated out. Anal. Calcd for $[\text{PPh}_4][\text{Pt}_3(\text{CO})_6]_6$: PPh₄, 13.04; Pt, 67.56; PPh₄:Pt, 1:9. Found: PPh₄, 13.54; Pt, 67.02; PPh₄:Pt, 1:8.6. (ν_{CO} (in THF) 2065 vs, 1900 sh, 1875 s, 1855 sh, 1840 sh cm^{-1} .)

3. Synthesis of the $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ Salts. (a) From $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and Sodium Acetate. $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1.97 g, 3.5 mmol) was added under carbon monoxide to a solution of 3.80 g (27.9 mmol) of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in methanol (35 ml). By 24 h stirring, the solution turned yellow-green and its infrared spectrum showed only carbonyl absorptions due to the $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ dianion (see Figure 2B). A solution of tetra-*n*-butylammonium chloride (1 g) in methanol (10 ml) was carefully stratified over the filtrated reaction solution and allowed to diffuse overnight. Blue-violet tiny crystals separated out in 70% yield. Anal. Calcd for $[\text{NBu}_4][\text{Pt}_3(\text{CO})_6]_5$: NBu₄, 11.38; Pt, 68.85; NBu₄:Pt, 1:7.5. Found: NBu₄, 11.9; Pt, 68.02; NBu₄:Pt, 1:7.1. (ν_{CO} (in THF) 2055 vs, 1890 mw, 1870 s, 1840 mw, 1830 sh cm^{-1} .)

(b) From $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and Sodium Hydroxide. Sodium hexachloroplatinate (1.65 g, 2.93 mmol) was added under carbon monoxide to a solution of 0.644 g (16.1 mmol) of sodium hydroxide in methanol (40 ml). By 24 h stirring, the reaction mixture turned yellow-green and separated out a white precipitate. After controlling the infrared spectrum, the suspension was filtered and tetra-*n*-butylammonium chloride (1 g) in methanol (10 ml) was added to the clear green solution. The resulting precipitate was separated by filtration, washed with methanol and dried under vacuum. The compound was crystallized by dissolution in acetone and precipitation by slow diffusion of isopropyl alcohol. Yield ca. 65%. The corresponding cesium, tetramethylammonium, tetraphenylphosphonium, tetraphenylarsonium, and bis(triphenylphosphine)iminium salts of the $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ dianion were prepared analogously by one of these two methods with yields up to ca. 80%. All these salts were fairly soluble in acetone, acetonitrile, and THF while, with the exception of the Cs, NMe₄ and NEt₄ were only sparingly soluble in methanol. They were crystallized by diffusion techniques from the couples of solvents acetone-isopropyl

alcohol or THF-toluene.

4. Synthesis of the $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ Salts. $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (3.05 g, 5.42 mmol) was added under carbon monoxide to a solution of 1.3 g (32.5 mmol) of sodium hydroxide in methanol (50 ml). By 24 h stirring, the solution turned blue-green and its ir spectrum showed only the carbonyl absorptions due to the $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ dianion (see Figure 2C). The reaction mixture was filtered and the solution was added to a solution of tetraphenylphosphonium bromide (1 g) in methanol (10 ml). The resulting brown precipitate was filtered, washed with methanol, and dried under vacuum. Crystallization by slow diffusion of toluene in concentrated THF solution afforded blue-black prisms of $[\text{PPh}_4][\text{Pt}_3(\text{CO})_6]_4$. Anal. Calcd for $[\text{PPh}_4][\text{Pt}_3(\text{CO})_6]_4$: PPh₄, 18.36; Pt, 63.42; PPh₄:Pt, 1:6. Found: PPh₄, 18.36; Pt, 63.42; PPh₄:Pt, 1:6.09. The corresponding Cs, NMe₄, NEt₄, *N-n*-Bu₄, AsPh₄, and PPN salts have been prepared in the same manner with yields up to ca. 80%. All these salts are fairly soluble in acetone, acetonitrile, and THF while, with the exception of the Cs, NMe₄ and NEt₄ are sparingly soluble in methanol. They have been crystallized from acetone-isopropyl alcohol or THF-toluene. (ν_{CO} (in THF) 2040 vs, 2030 sh, 1880 mw, 1860 s, 1825 mw cm^{-1} .)

5. Synthesis of the $[\text{Pt}_3(\text{CO})_6]_3^{2-}$ Salts. Sodium hexachloroplatinate(IV) (3.06 g, 5.44 mmol) was added to a solution of 1.97 g (49.2 mmol) of sodium hydroxide in methanol (50 ml). By 24 h stirring under carbon monoxide, a violet-red solution was obtained whose ir spectrum showed only carbonyl absorptions due to the $[\text{Pt}_3(\text{CO})_6]_3^{2-}$ dianion (see Figure 2D). The suspension was filtered under nitrogen and a solution of tetraethylammonium chloride (1 g) in methanol (10 ml) was added. The resulting brown precipitate was filtered, washed with methanol, and dried under vacuum. Crystallization by slow diffusion of toluene in concentrated THF solution afforded 1.02 g of dark red prisms. Anal. Calcd for $[\text{NEt}_4][\text{Pt}_3(\text{CO})_6]_3$: NEt₄, 10.32; Pt, 69.68; CO, 20.00; NEt₄:Pt:CO, 1:4.5:9. Found: NEt₄, 10.44; Pt, 68.94; CO, 20.02; NEt₄:Pt:CO, 1:4.41:8.94. The corresponding NMe₄, *N-n*-Bu₄, PPh₄, AsPh₄, and PPN salts have been prepared in the same way with yields up to 80%. All these salts are fairly soluble in acetone, acetonitrile, and THF and have been crystallized by slow diffusion in acetone-isopropyl alcohol, acetonitrile-diisopropyl ether, and THF-toluene. (ν_{CO} (in THF) 2030 vs, 1855 sh, 1840 s, 1830 sh, 1810 m cm^{-1} .)

6. Synthesis of the $[\text{Pt}_3(\text{CO})_6]_2^{2-}$ Salts. (a) From $[\text{N-n-Bu}_4][\text{Pt}_3(\text{CO})_6]_4$. $[\text{N-n-Bu}_4][\text{Pt}_3(\text{CO})_6]_4$ (1.73 g) was dissolved in anhydrous THF (30 ml) and reacted under carbon monoxide with lithium metal. By 12 h stirring, the blue-green solution turned orange-red and its ir spectrum showed only carbonyl absorptions due to the $[\text{Pt}_3(\text{CO})_6]_2^{2-}$ dianion (see Figure 2E). The suspension was filtered under nitrogen and evaporated to dryness. The residue was dissolved in methanol (20 ml) and precipitated by addition of solid tetraphenylphosphonium bromide. The dark red precipitate was filtered, washed with methanol, and dried under vacuum. Crystallization from THF-toluene gave 0.87 g of dark red prisms. Anal. Calcd for $[\text{PPh}_4][\text{Pt}_3(\text{CO})_6]_2$: PPh₄, 31.03; Pt, 53.58; PPh₄:Pt, 1:3. Found: PPh₄, 30.82; Pt, 53.32; PPh₄:Pt, 1:3.

(b) From $\text{Pt}(\text{CO})_2\text{Cl}_2$. $\text{Pt}(\text{CO})_2\text{Cl}_2$ (2.5 g) was dissolved in anhydrous THF (30 ml) at -70°C and reacted under carbon monoxide with lithium metal in excess. By raising the temperature to 25°C a vigorous reaction took place and a brilliant green color developed. After 2 h stirring the solution turned violet-red and then slowly orange-red. The suspension was stirred until the ir spectrum showed only the presence of $[\text{Pt}_3(\text{CO})_6]_2^{2-}$. The suspension was filtered under nitrogen and added to a solution of cesium chloride (0.5 g) in water (25 ml). Concentration under vacuum gave 0.81 g of tiny dark red crystals. They were separated by filtration, washed with water, and dried under vacuum. Anal. Calcd for $\text{Cs}_2[\text{Pt}_3(\text{CO})_6]_2$: Cs, 15.0; Pt, 66.04; CO, 18.95; Cs:Pt:CO, 1:3:6. Found: Cs, 15.6; Pt, 67.42; CO, 18.13; Cs:Pt:CO, 1:2.97:5.52. (ν_{CO} (in THF) 1995 vs, 1818 m, 1795 s cm^{-1} .)

7. Synthesis of $\text{K}_2[\text{Pt}_3(\text{CO})_6]$. $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ (0.61 g) was suspended in anhydrous THF (20 ml) and reacted under carbon monoxide with 2 ml of sodium-potassium alloy (K = 80%). Under vigorous stirring the $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ slowly dissolved to give a green solution which in 3 h turned first violet-red, then orange-red, and finally pink-red. The suspension was stirred until the ir spectrum showed only carbonyl absorptions due to the $[\text{Pt}_3(\text{CO})_6]_2^{2-}$ dianion. Any attempt to precipitate the product gave mainly decomposition. Analysis of this solution shows a relative ratio Pt:(Na + K) = 1.59. (ν_{CO} (in THF) 1945 vs, 1740 s cm^{-1} .)

8. Reaction of $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ with NaI. (a) In Methanol.

$\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ (0.26 g) was suspended in methanol (10 ml) and reacted under carbon monoxide with sodium iodide (0.35 g). By vigorous stirring the $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ slowly dissolved to give a yellow-green solution whose ir spectrum showed the presence of the $[\text{Pt}_3(\text{CO})_6]_5^{2-}$ dianion. After 4 h stirring the suspension was filtered and precipitated by addition of a concentrated solution of tetraethylammonium chloride in methanol (10 ml). The resulting green-violet precipitate was filtered, washed with aqueous methanol, and dried under vacuum (yield 0.15 g).

(b) In THF. $\text{Na}_2[\text{Pt}_3(\text{CO})_6]_{10}$ (0.302 g) was suspended in anhydrous THF (10 ml) and reacted under carbon monoxide with 0.2 g of sodium iodide. By vigorous stirring the suspension turned blue-green and the ir spectrum showed the presence of the $[\text{Pt}_3(\text{CO})_6]_4^{2-}$ dianion. After 3 h stirring, the suspension was filtered and evaporated to dryness under vacuum. The residue was dissolved in methanol (15 ml) and solid tetraphenylphosphonium chloride was added to give 0.21 g of $[\text{PPh}_4]_2[\text{Pt}_3(\text{CO})_6]_4$.

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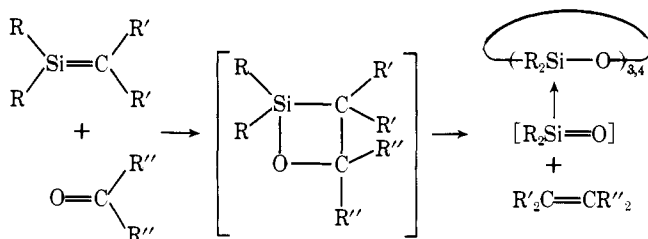
Reaction of a Disilene and Benzaldehyde¹

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Abstract: Tetramethyldisilene, $\text{Me}_2\text{Si}=\text{SiMe}_2$, was generated from the decomposition of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes⁴ at 480–500 °C in a flow system in the presence of excess benzaldehyde. The major products are *trans*-stilbene, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane. While these products clearly implicate the intermediacy of dimethylsilanone, $\text{Me}_2\text{Si}=\text{O}$, its origin is unclear. Several mechanistic possibilities were examined. That both stilbene and dimethylsilanone arise from a single, common intermediate, 5,6-diphenyl-2,2,3,3-tetramethyl-2,3-disiladioxane (**12**), must be considered as a mechanistic possibility.

In recent years it has been amply demonstrated that transient silenes ($\text{R}_2\text{Si}=\text{CR}'_2$) are very efficiently trapped by the carbonyl group of aldehydes and ketones.² It is generally agreed that this reaction proceeds through cycloaddition of the silene to the carbonyl group to produce an unstable silaoxetane



which thermally decomposes to an olefin and a silanone ($\text{R}_2\text{Si}=\text{O}$) which undergoes cyclic oligomerization. This initial addition is in accord with the predictions of Curtis³ that silenes should be highly polar, $\text{R}_2\text{Si}^{\delta+}=\delta-\text{CR}_2$.

In contrast to the rather extensive studies of the chemistry of the silicon-carbon double bond,² very little is known about the behavior of disilenes, $\text{R}_2\text{Si}=\text{SiR}_2$. Roark and Peddle⁴ have reported strong evidence that 7,8-disilabicyclo[2.2.2]octa-2,5-dienes, **1** and **2**, thermally aromatize through extrusion of a disilene. The descriptive chemistry of disilenes has been limited to a few Diels-Alder reactions, internal rearrangements,⁴ and the addition to an alkyne.⁵ We have begun to examine the reactions of disilenes with various possible trapping reagents. In view of the above mentioned efficiency of silene trapping by ketones and aldehydes, the carbonyl group is an