

The Carbonyls of the Platinum Group Metals

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In recent years improved methods of synthesis have made it possible for the chemistry of the carbonyls of the platinum group metals to be studied more thoroughly. This article reviews the preparation, structure, chemical reactions and uses of these important and interesting compounds.

Complexes where the carbonyl group is the only ligand present have been reported for all the platinum group metals except palladium. These compounds are listed in the table.

The colourless volatile ruthenium and osmium pentacarbonyls are unstable in ultraviolet light at room temperature and decompose to give the trinuclear dodecacarbonyls. Recently irradiation of $\text{Os}(\text{CO})_5$ at -40°C has led to the isolation of $\text{Os}_3(\text{CO})_9$ (1). The analogous ruthenium compound has not yet been prepared although the iron compound $\text{Fe}_2(\text{CO})_9$ has been known for many years.

The existence of $\text{Rh}_2(\text{CO})_8$ and $\text{Ir}_2(\text{CO})_8$ analogous to the cobalt carbonyl $\text{Co}_2(\text{CO})_8$ was claimed by early workers in this field but attempts by others to repeat the original preparations have been unsuccessful. All that has been obtained is some infrared spectral evidence for the reversible formation of $\text{Rh}_2(\text{CO})_8$ from $\text{Rh}_4(\text{CO})_{12}$ under high pressure of carbon monoxide at low temperature (-19°C).

No substantiated reports have been published on platinum or palladium compounds similar to the nickel carbonyl $\text{Ni}(\text{CO})_4$. Thus the polymeric platinum dicarbonyl is the only known carbonyl of these two metals and even this compound is unstable in air.

A number of heteronuclear platinum metal carbonyls have also been prepared recently, e.g., $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$.

Methods of Preparation

Until recently all the preparative methods with the exception of that for $\text{Pt}_n(\text{CO})_{2n}$ involved the use of carbon monoxide at moderately high pressures (10 to 200 atm).

The recommended method for the preparation of $\text{Ru}_3(\text{CO})_{12}$ is to treat ruthenium acetylacetonate in methanol solution with a 3:1 mixture of carbon monoxide and hydrogen at 160 atm pressure at 165°C (2). The preparation can be simplified by preparing the ruthenium acetylacetonate in situ by using ruthenium trichloride hydrate and sodium acetylacetonate. $\text{Os}_3(\text{CO})_{12}$ can be prepared

Carbonyls of the Platinum Group Metals

$\text{Ru}(\text{CO})_5$ Colourless m.p. -22°C	$\text{Rh}_4(\text{CO})_{12}^*$ Red dec. $130-140^\circ\text{C}$	
$\text{Ru}_3(\text{CO})_{12}^*$ Orange m.p. 153°C	$\text{Rh}_6(\text{CO})_{16}^*$ Black dec. $197-208^\circ\text{C}$	
$\text{Os}(\text{CO})_5$ Colourless m.p. -15°C	$\text{Ir}_4(\text{CO})_{12}$ Yellow dec. 230°C	$\text{Pt}_n(\text{CO})_{2n}$ Cherry-red
$\text{Os}_2(\text{CO})_9$ Orange-yellow dec. $64-67^\circ\text{C}$	$\text{Ir}_6(\text{CO})_{16}$ Red	
$\text{Os}_3(\text{CO})_{12}^*$ Yellow m.p. 220°C		

m.p. = melting point dec. = decomposes

* These compounds are now available from Johnson Matthey & Co. Limited.

by treating OsO_4 in methanol (3) or xylene (4) solution with carbon monoxide at 175 atm, 175°C . The pentacarbonyls $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ can both be obtained by the above methods using heptane as solvent. This increases the yield of the pentacarbonyls and decreases that of the dodecacarbonyls (5).

Recently $\text{Ru}_3(\text{CO})_{12}$ has been prepared by passing a stream of carbon monoxide through a solution of ruthenium trichloride hydrate in refluxing 2-ethoxy-ethanol to give a ruthenium carbonyl chloride solution, which was further carbonylated to the dodecacarbonyl by addition of zinc and ethanol and continuation of the refluxing and treatment with carbon monoxide (6). An alternative atmospheric synthesis is to pass carbon monoxide through a propanol solution containing ruthenium oxoacetate $[\text{Ru}_3\text{O}(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_3]\text{O}_2\text{CCH}_3$ and a base such as triethylamine at 85°C (7).

The two rhodium cluster carbonyls were first prepared by reduction of anhydrous rhodium trichloride with carbon monoxide at 200 atm using a metal (e.g., copper, zinc or silver) as halogen acceptor. At temperatures of $50\text{--}80^\circ\text{C}$ the main product was $\text{Rh}_4(\text{CO})_{12}$ whereas at $80\text{--}230^\circ\text{C}$ the only product was $\text{Rh}_6(\text{CO})_{16}$. More recently $\text{Rh}_4(\text{CO})_{12}$ has been prepared at atmospheric pressure and room temperature in aqueous solution by reduction of $[\text{RhCl}_6]^{3-}$ to $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ with copper metal and carbon monoxide, followed by further reduction with carbon monoxide and water in the presence of sodium citrate buffer (8). $\text{Rh}_6(\text{CO})_{16}$ has also been prepared under similar mild conditions by reducing $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with carbon monoxide in water-alcohol solution in the presence of lithium acetate (9).

The iridium carbonyl $\text{Ir}_4(\text{CO})_{12}$ can be prepared in 50 to 60 per cent yield by reacting iridium trichloride with carbon monoxide under pressure in aqueous methanol solution in the presence of sodium bicarbonate (10). Reduction of a suspension of $\text{Ir}_4(\text{CO})_{12}$ in tetrahydrofuran with sodium yields first the anion $[\text{Ir}_4(\text{CO})_{11}\text{H}]^-$, then $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ and finally $[\text{Ir}(\text{CO})_4]^-$. If the intermediate

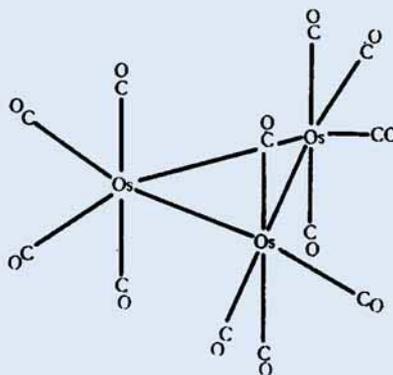


Fig. 1 Structure of $\text{Os}_3(\text{CO})_{12}$. The structure of $\text{Ru}_3(\text{CO})_{12}$ is similar. (Figs. 1-4 after Abel and Stone)

hexairidium ion is isolated as the tetraethylammonium salt and suspended in acetic acid in a carbon monoxide atmosphere for several days the neutral red carbonyl $\text{Ir}_6(\text{CO})_{16}$ is precipitated (11).

The unstable polymeric platinum dicarbonyl $\text{Pt}_n(\text{CO})_{2n}$ has been obtained as a cherry red precipitate by the action of carbon monoxide on aqueous (12) or ethanolic (13) solutions of Pt^{II} compounds (e.g. K_2PtCl_4) at temperatures up to 80°C ; or as a purple colloidal precipitate by the action of water on a benzene solution of $\text{Pt}(\text{CO})_2\text{Cl}_2$ under an atmosphere of carbon monoxide (13).

Structures

The infrared spectra of $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$ suggest that they both have the same trigonal bipyramidal structure as $\text{Fe}(\text{CO})_5$.

In crystalline $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ the metal atoms form an equilateral triangle, each being bound to four terminal carbonyl groups, two approximately perpendicular to and two parallel to the plane of the triangle (Fig. 1). The mixed metal carbonyls $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$ probably have similar structures. It is interesting to note that in $\text{Fe}_3(\text{CO})_{12}$ two of the iron atoms are bridged by two carbonyl groups. The absence of bridging carbonyl groups in the ruthenium and osmium compounds, in which

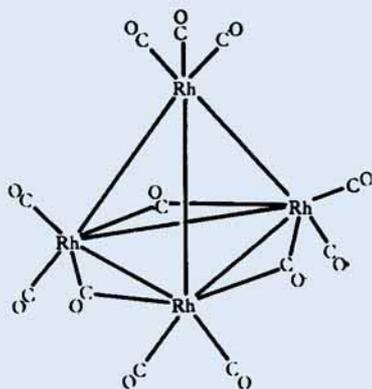


Fig. 2 Structure of $Rh_4(CO)_{12}$

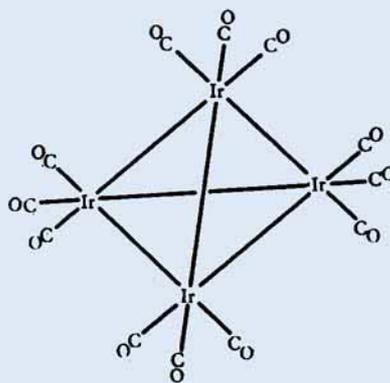


Fig. 3 Structure of $Ir_4(CO)_{12}$

the triangular cluster is held together by metal-metal bonds alone, is indicative of the increase in the strength of metal-metal bonds on going down a transition metal triad.

The structures of $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$ are shown in Figs. 2 and 3; that of the rhodium compound is similar to $Co_4(CO)_{12}$. Thus in this triad the transition from a carbonyl bridged to a non-bridged structure occurs between the 2nd and 3rd row transition elements and not between the 1st and 2nd row elements as in the iron group triad.

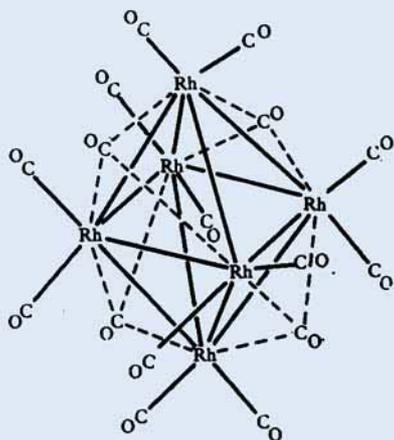


Fig. 4 Structure of $Rh_6(CO)_{16}$

The structure of $Rh_6(CO)_{16}$ is shown in Fig. 4. Four of the carbonyl groups are bridging three rhodium atoms.

It is thought that the platinum carbonyl $Pt_n(CO)_{2n}$ is monomeric in solution but pentameric in the solid state (12).

Bonding in Metal Carbonyls

The ability of the carbonyl group to stabilise metal atoms in low positive, zero, or low negative oxidation states is believed to be due to the fact that the carbonyl group not only donates a lone pair of electrons to form a σ bond but can also accept back electrons to form a π bond. More specifically there is first a dative overlap of the filled carbon σ orbital with an empty metal σ orbital and second a dative overlap of a filled $d\pi$ or hybrid $dp\pi$ metal orbital with an empty antibonding $p\pi$ orbital of the carbon monoxide (Fig. 5).

The effect is synergic as the drift of electrons to the metal in the σ bond tends to make the CO positive, thus enhancing the acceptor strength of the π orbitals. Similarly, the drift of metal electrons into CO π orbitals tends to make the CO negative and hence increase its basicity via the carbon σ orbital.

Carbonyls bridging two metal atoms are considered to be similar to organic keto-type bridges. The carbon forms sp^2 σ orbitals which means that there can be only one C-O

π bond. The metal-carbon π bonding is more complicated than with terminal carbonyl groups and may be multicentre in character. For carbonyl groups which bridge three metal atoms simultaneously no simple picture is possible and multicentre bonding must be invoked with bonding electrons assigned to molecular orbitals.

Reactions

During the last five years the reactions of the noble metal carbonyls, especially those of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$, have been investigated in some detail. The most notable feature is the stability of the metal atom clusters and the increase in this stability on going from the second to the third row transition elements.

All the carbonyls react with neutral ligands such as triphenylphosphine to give substituted species. Whereas with $\text{Ru}_3(\text{CO})_{12}$ only the trisubstituted compounds $\text{Ru}_3(\text{CO})_9\text{L}_3$ (L=phosphine ligand) have been isolated, in the case of $\text{Os}_3(\text{CO})_{12}$ all three derivatives $\text{Os}_3(\text{CO})_{12-x}\text{L}_x$ ($x=1-3$) are obtained. In these compounds only one carbonyl group is substituted on any one metal atom. Further work with $\text{Os}_3(\text{CO})_{12}$ using less PPh_3 has led to the separation of six more products in which there are examples of bridging PPh_3 groups, bridging phenyl groups, co-ordinated "benzyne" C_6H_4 , and loss of hydrogen atoms from phenyl groups

with concomitant formation of Os-C σ bonds.

The tetra- and hexa-rhodium carbonyls react to give $\text{Rh}_4(\text{CO})_{12-x}\text{L}_x$ ($x=1-4$) and $\text{Rh}_6(\text{CO})_{16-x}\text{L}_x$ ($x=6$ or 9) respectively, although the reactions may easily be taken further to $\text{Rh}_2(\text{CO})_4\text{L}_4$.

$\text{Ir}_4(\text{CO})_{12}$ reacts to form $\text{Ir}_4(\text{CO})_{12-x}\text{L}_x$ ($x=2, 3$). The structures of the substituted derivatives differ from the parent carbonyl by having three bridging carbonyl groups.

Substituted products have also been obtained with bidentate ligands and in instances where crystal structures have been determined the ligands bridge adjacent metal atoms.

The reactions of the trinuclear carbonyls $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ differ significantly towards halogens. At low temperatures $\text{Ru}_3(\text{CO})_{12}$ gives *cis* $\text{Ru}(\text{CO})_4\text{X}_2$ (X=halogen) which on warming trimerises to $\text{Ru}_3(\text{CO})_{12}\text{X}_6$; this loses carbon monoxide to give $[\text{Ru}(\text{CO})_3\text{X}_2]_2$ which on pyrolysis under vacuum at 200°C goes to $[\text{Ru}(\text{CO})_2\text{X}_2]_n$.

With $\text{Os}_3(\text{CO})_{12}$, however, one Os-Os bond is initially ruptured to give $\text{Os}_3(\text{CO})_{12}\text{X}_2$. This compound loses two molecules of carbon monoxide on refluxing in benzene for 24 hours giving $\text{Os}_3(\text{CO})_{10}\text{X}_2$ in which the two halogen atoms bridge the two osmium atoms which have lost the carbonyl groups. Further chlorination of $\text{Os}_3(\text{CO})_{10}\text{Cl}_2$ breaks the remaining Os-Os bonds yielding a mixture of $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ and *cis* $\text{Os}(\text{CO})_4\text{Cl}_2$.

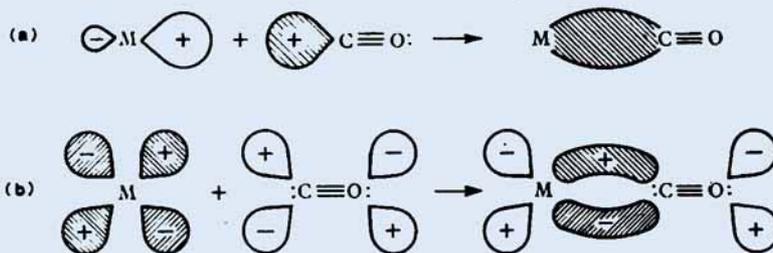


Fig. 5 (a) The formation of the metal←carbon σ bond using an unshared pair on the carbon atom. (b) The formation of the metal→carbon π bond. The other orbitals on the carbonyl group are omitted for clarity. (After Cotton and Wilkinson)

The two rhodium carbonyls react with halogens to give $\text{Rh}_2(\text{CO})_4\text{X}_6$.

The type of structure exhibited by $\text{Os}_3(\text{CO})_{10}\text{Cl}_2$ has been found to be quite common among the derivatives of the trinuclear carbonyls. For example, thiols, RSH , react to give $\text{HM}_3(\text{CO})_{10}(\text{SR})_3$ ($\text{M}=\text{Os}, \text{Ru}$) which contain bridging hydride and SR groups, and $\text{Os}_3(\text{CO})_{12}$ reacts with Ph_3PAuCl to give $\text{Os}_3(\text{CO})_{10}(\text{AuPPh}_3)\text{Cl}$ with bridging chlorine and AuPPh_3 groups.

Reactions with other metal halides give different results, however. Stannic chloride reacts at room temperature giving $\text{M}_3(\text{CO})_{12}(\text{SnCl}_3)\text{Cl}$, while mercuric halides in boiling xylene form $\text{M}(\text{CO})_4(\text{HgX})_2$.

The rhodium carbonyls react with thiols to give thiolato bridged dimers $\text{Rh}_2(\text{CO})_4(\text{SR})_2$, the tetra-rhodium carbonyl reacting at room temperature and the hexarhodium carbonyl in boiling toluene.

Both the trinuclear carbonyls can be protonated by concentrated sulphuric acid to give the cations $[\text{HM}_3(\text{CO})_{12}]^+$ ($\text{M}=\text{Ru}, \text{Os}$) which have been isolated as the $[\text{PF}_6]^-$ salts. The cations decompose on heating to give $[\text{HM}(\text{CO})_6]^+$ which can also be obtained by direct protonation of $\text{M}(\text{CO})_6$.

$\text{Rh}_4(\text{CO})_{12}$ decomposes in cold concentrated sulphuric acid but $\text{Rh}_6(\text{CO})_{18}$ dissolves to give a cationic species. $\text{Ir}_4(\text{CO})_{12}$ dissolves slowly at room temperature to give a stable protonated species which has been formulated as $[\text{H}_3\text{Ir}_4(\text{CO})_{12}]^{2+}$. Attempts to isolate solid $[\text{PF}_6]^-$ salts of the hexarhodium and tetrairidium cations have not been successful.

Reaction of potassium hydroxide in methanol with $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ gives anionic species which on acidification form the hydridocarbonyls $\text{H}_4\text{M}_4(\text{CO})_{12}$, $\text{H}_2\text{M}_4(\text{CO})_{13}$, $\text{HOs}_3(\text{CO})_{10}(\text{OH})$ and $\text{H}_2\text{Os}_3(\text{CO})_{10}$.

Under reflux in carboxylic acids $\text{Ru}_3(\text{CO})_{12}$ reacts to give $[\text{Ru}(\text{CO})_2(\text{RCO}_2)]_n$. The acetate forms the dimer $[\text{Ru}(\text{CO})_3(\text{CH}_3\text{CO}_2)]_2$ on reaction with carbon monoxide under pressure. With $\text{Os}_3(\text{CO})_{12}$ the dimer is obtained directly by reaction in a sealed tube

at 170°C . $\text{Rh}_6(\text{CO})_{18}$ reacts slowly with acetic acid to give $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CO}_2)]_2$ and metallic rhodium.

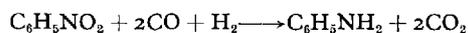
Reaction of the trinuclear ruthenium and osmium carbonyls with acetylenes leads to the formation of numerous mono-, bi- and trinuclear compounds. Eight derivatives have been isolated from the reaction of $\text{Ru}_3(\text{CO})_{12}$ with diphenylacetylene and one of these $\text{Ru}_3(\text{CO})_8[\text{PhC}_2\text{Ph}]_2$ exists as two isomers, one containing a Ru_3 cluster with no bridging carbonyls which is easily transformed to a more stable isomer having a metallacyclopentadiene ring and bridging carbonyl groups.

Reaction of $\text{M}_3(\text{CO})_{12}$ with silanes, stannanes and germanes ($\text{R}_3\text{M}'\text{X}$), ($\text{M}'=\text{Si}, \text{Sn}, \text{Ge}$), under various conditions leads to the formations of compounds of the general formula $(\text{R}_3\text{M}')_2\text{M}(\text{CO})_4$ and in the case of osmium the hydrides $\text{R}_3\text{M}'\text{Os}(\text{CO})_4\text{H}$. Dimeric species such as $[\text{R}_3\text{SiOs}(\text{CO})_4]_2$ and $[(\text{Me}_3\text{Sn})\text{Ru}(\text{CO})_3(\text{SnMe}_2)]_2$ are also obtained. In the latter compound the two ruthenium atoms are bridged by two SnMe_2 groups.

Uses of the Carbonyls

As well as being the starting materials for the preparation of many other compounds as described above, these carbonyls, especially the ruthenium and rhodium compounds, act as catalysts in a number of organic syntheses.

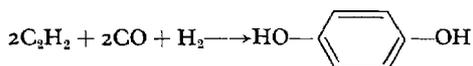
For example, $\text{Ru}_3(\text{CO})_{12}$ promotes the homogeneous reduction of nitrobenzene to aniline by carbon monoxide and hydrogen at 200 atm, 160°C (14). Yields in the order of 66 per cent are obtained. The stoichiometry of the reaction is probably:



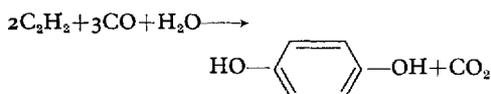
At $\text{CO}:\text{H}_2$ ratios higher than 1, diphenylurea is formed as a byproduct. A reaction mechanism has been proposed in which a phenylnitrene intermediate stabilised by bonding to ruthenium undergoes either hydrogenolysis to give aniline or carbon monoxide insertion and hydrogenolysis to give 2,2' diphenylurea. Other nitro com-

pounds have been similarly reduced to amines.

$\text{Ru}_3(\text{CO})_{12}$ also catalyses the carbonylation of acetylene to hydroquinone (15). Yields of 60 per cent are obtained in tetrahydrofuran solution at 200°C using 120 atm carbon monoxide plus 10 atm hydrogen.



Water or alcohol can also be used as the source of hydrogen and similar yields of hydroquinone obtained.



A third example of the catalytic activity of $\text{Ru}_3(\text{CO})_{12}$ is in the hydroformylation of olefins. A typical reaction is the conversion of propylene to butyraldehyde which proceeds at a good rate at 150°C with carbon monoxide and hydrogen under pressure to give 70 per cent yields (16).

The two rhodium carbonyls have also been used as hydroformylation catalysts, e.g. $\text{Rh}_4(\text{CO})_{12}$ for the hydroformylation of 1-heptene at 75°C , 40 atm (17), and $\text{Rh}_6(\text{CO})_{16}$ for the hydroformylation of cyclohexene (18).

It is not always the carbonyl alone that is used as the catalyst. For example, $\text{Rh}_6(\text{CO})_{16}$ together with PPh_3 catalyses the 100 per cent conversion of 1-hexene to a mixture of 2-methylhexaldehyde (27 per cent) and *n*-heptaldehyde (73 per cent) by reaction with with a 1:1 mixture of carbon monoxide and hydrogen at 82°C , 35 atm (19).

There are fewer examples of the use of the osmium and iridium carbonyls as catalysts. However, these compounds will probably be important in studying the course of reactions, the slower reaction rates enabling intermediates to be isolated.

Although no catalytic uses of $\text{Pt}_n(\text{CO})_{2n}$ as such have been described in the literature it has been postulated that carbomethoxy derivatives of platinum carbonyls are catalytically active in the electrochemical synthesis of methyl esters of α , β unsaturated carboxylic

acids from olefins under 70 atm carbon monoxide (20). The platinum compounds are formed by electrolysis under carbon monoxide pressure of a solution of sodium methoxide in methanol using platinum electrodes.

It is hoped that now a number of the platinum group metal carbonyls are more readily available further uses will be found both for the carbonyls themselves and for their derivatives.

References

References have only been given for the methods of preparation and the uses of the platinum metal carbonyls. For further details of the reactions of metal carbonyls in general the excellent reviews of E. W. Abel and F. G. A. Stone in *Quarterly Reviews* (1969, 23, 325 and 1970, 24, 498) are recommended.

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