

SOME ASPECTS OF THE CHEMISTRY OF POLYNUCLEAR METAL CARBONYL COMPOUNDS

P. CHINI

*Istituto di Chimica Generale ed Inorganica dell'Università,
Via G. Venezian 21, 20133 Milano, Italy*

ABSTRACT

The reactions of metal carbonyl clusters are classified in: (a) photolysis, pyrolysis and S_N1 substitutions, (b) oxidation and reactions with electrophilic reagents, (c) reduction and (d) nucleophilic attack.

For a qualitative discussion of the electronic spectra and of some S_N1 reactions the presence of molecular orbitals having both metal-metal and metal-carbon character, which are delocalized over the whole cluster, is assumed. Such a delocalized situation, formally similar to that of organic aromatic compounds, also agrees with the reactivity of the carbonyl clusters toward electrophilic agents and with facile reduction by alkali metals. On the contrary some common examples of reactions with nucleophilic agents are discussed considering a localized attack on the carbon atom of a carbonyl group, analogous to that observed with organic carbonyl compounds.

INTRODUCTION

Metal cluster compounds are one of the fields of inorganic chemistry which is expanding most rapidly, and it has been recently reviewed more than once¹⁻⁷. Still it is the unusual structures of such compounds, and the bonding problems which they raise, rather than their chemical properties, which have stimulated interest. Hence it seems appropriate to attempt a discussion of basic types of reactions of the polynuclear metal carbonyls. Due to the complexity of the compounds a detailed discussion of mechanisms is very difficult, and only some general trends will be pointed out. Such trends are of interest both in synthesis and chemical characterization of the compounds, two aspects of the same chemical problem often largely artificially separated.

Reactions of the polynuclear metal carbonyls can be classified according to the type of electron transfer in the first reaction step: electrons can be added, subtracted or transferred from the frontier orbitals of the cluster. Photolysis and pyrolysis involve transfer of electrons from the last bonding orbital, a process which may also be assumed in S_N1 substitutions. Subtraction of electrons from the last bonding orbital is the key step in oxidation and addition of electrophilic reagents. Addition of electrons to the anti-bonding frontier orbital is common to both reduction and nucleophilic attack.

The presence of carbon monoxide allows considerable changes in the

electron density of a cluster by adjusting back-donation between carbon monoxide groups and metal atoms. For instance, if an electrophilic reagent reacts with a cluster, there can be partial motion of negative charge from the bonding frontier orbital towards the reagent, and the carbonyl groups can compensate this change by a minor degree of back-donation. Conversely, if a nucleophilic reagent reacts with a cluster, negative charge is added at the frontier antibonding orbital, but carbonyl groups can again favour reaction by allowing better back-donation. The presence of carbonyl groups can therefore offset changes in electron density, and favour the reactivity of the polynuclear metal carbonyl derivatives with respect to both electrophilic and nucleophilic reagents.

A decrease in the separation of frontier orbitals would be expected to favour reactions involving either transfer, addition or subtraction of electrons, a result very similar to that observed in organic chemistry with increasing conjugation between multiple bonds. The trend of electronic spectra can be reasonably assumed to reflect the separation of frontier orbitals; the absorption bands are generally found shifted in the direction of lower energy on increasing the number of cluster metal atoms. This trend is clearly in evidence with the colours and ultra-violet spectra of the carbonylferrates⁸, as well as in the colour sequences found with other carbonylmetallates, e.g. carbonylrhodates (*Table 1*)⁹.

Table 1. Colours and electronic spectra of some carbonylmetallates.

Carbonylferrates ⁸	λ_{\max} , m μ	Colour	Carbonylrhodates ⁹	Colour
[Fe(CO) ₄] ²⁻	300	Colourless	[Rh(CO) ₄] ⁻	Colourless
[Fe ₂ (CO) ₈] ²⁻	347	Orange	[Rh ₃ (CO) ₁₀] ⁻	Yellow
[Fe ₃ (CO) ₁₁] ²⁻	485	Red	[Rh ₆ (CO) ₁₄] ⁴⁻	Red-brown
[Fe ₄ (CO) ₁₃] ²⁻	500	Brown	[Rh ₇ (CO) ₁₆] ³⁻	Dark green
			[Rh ₁₂ (CO) ₃₀] ²⁻	Violet

Obviously the limiting case is that of continuous absorption by pure metals, which is also associated with a high delocalization of bonding electrons. In the case of cluster compounds occurrence of delocalization has been proved by Dahl and co-workers in a study of metal-metal interatomic distances in analogous diamagnetic and paramagnetic compounds such as $(\pi\text{-Cp})_3\text{Ni}_2\text{Co}(\text{CO})_2$ and $(\pi\text{-Cp})_3\text{Ni}_3(\text{CO})_2$. The addition of one electron in the antibonding frontier orbital brings about lengthening of all metal-metal interatomic distances proving that this electron is present on a highly delocalized molecular orbital¹⁰. The consideration of delocalized metal-metal bonds is also useful for explaining unusual stereochemical situations, such as those found in the six-metal-atom carbonyl clusters⁶.

Comparison of electronic spectra of similar clusters in a subgroup shows increased frequencies of absorption, a trend which proceeds parallel to lightening of colour and increase in thermal stability (*Table 2*)^{11,12}.

The increased frequency of absorption which is found in homologous clusters when descending the subgroups can be due to lower order in metal-metal interactions, or in other words to decrease in the multiple character

CHEMISTRY OF POLYNUCLEAR METAL CARBONYL COMPOUNDS

 Table 2. Colours, electronic spectra and decomposition temperatures of the $M_3(CO)_{12}$ and $M_4(CO)_{12}$ clusters^{11, 12}

Compound	λ_{\max} , m μ	Colour	Dec. point, °C
Fe ₃ (CO) ₁₂	597 ¹¹	Dark green	140
Fe ₂ Ru(CO) ₁₂	548 ¹¹	Purple	125
FeRu ₂ (CO) ₁₂	476 ¹¹	Red-orange	140
Ru ₃ (CO) ₁₂	392 ¹¹	Red-orange	150
Os ₃ (CO) ₁₂	—	Yellow	> 224
Co ₄ (CO) ₁₂	375 ¹²	Dark brown	100
Co ₃ Rh(CO) ₁₂	365 ¹²	Brown	130–135
Co ₂ Rh ₂ (CO) ₁₂	348 ¹²	Brown	120
Rh ₄ (CO) ₁₂	300 ¹²	Red	130–140
Rh ₃ Ir(CO) ₁₂	300 ¹²	Orange	130–170
Ir ₄ (CO) ₁₂	319 ¹²	Yellow	210

of metal-metal bonds. This would correspond to less delocalization and a more discontinuous system of energy levels. In favour of this interpretation is the fact that the specific electronic heat of the pure metals, usually γ , exhibits an analogous decrease in the subgroup (Table 3).

 Table 3. Metal-metal distances¹⁷ (d , Å), atomization energies¹⁸ (H^0 , kcal/g), specific electronic heats¹³ (γ , mjoules/g atom K) and lattice type (bcc: body centred cube, hc: hexagonal compact; cc: cubic compact)¹⁹ of Group VIII metals

Fe		Co		Ni	
d 2.48	2.46–2.88 (in clusters)	d 2.51	2.46–2.64 (in clusters)	d 2.49	2.36–2.51 (in clusters)
H^0 96.98	γ 5.02 bcc	H^0 105	γ 4.75 hc-cc	H^0 101.6	γ 7.28 cc
Ru		Rh		Pd	
d 2.65	2.78–2.93 (in clusters)	d 2.69	2.62–2.94 (in clusters)	d 2.75	
H^0 160	γ 3.35 hc	H^0 138	γ 4.89 cc	H^0 93	γ 9.9 cc
Os		Ir		Pt	
d 2.675	2.76–2.88 (in clusters)	d 2.71	2.68–2.73 (in clusters)	d 2.775	2.65–2.79 (in clusters)
H^0 174	γ 2.35 hc	H^0 165	γ 3.51 cc	H^0 121.6	γ 6.63 cc

It has been pointed out that metal-metal bond distances are the best index when comparing metal-metal bonds². Distances in pure metals often resemble those in cluster carbonyl compounds (Table 3), which indicates that a comparison of other properties is also possible. The specific electronic heat γ is directly proportional to the state density at the Fermi surface and, in a subgroup of elements crystallizing with the same lattice, is directly related to the number of interactions of the metal orbitals^{13, 14}. Probably this decrease in number of interactions reflects the decreased repulsion between electrons of the same orbital. It is well known that pairs of electrons

become more inert on increasing the dimensions of the orbital, as occurs in the final metals of the last period.

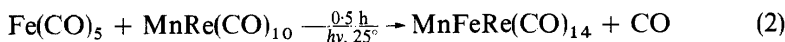
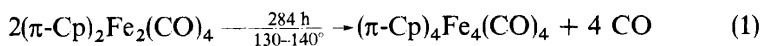
In the pure metals, as shown by the standard atomization energies, metal-metal bond energies increase in the subgroup^{14,15}. This increase is probably due to the progressive minor penetration of $(n - 1)d$ orbitals into the core and associated better overlapping. An analogous increase in bond energies has been observed in carbonyl clusters: in mass spectroscopy the three metal atom ions amount to 35 per cent with $\text{Fe}_3(\text{CO})_{12}$, 92 per cent for $\text{Ru}_3(\text{CO})_{12}$ and 100 per cent¹⁶ for $\text{Os}_3(\text{CO})_{12}$.

In conclusion separation between the frontier orbitals increases on passing down a subgroup, while at the same time the metal-metal bond strength increases. The first factor decreases reactivity; the polynuclear metal carbonyls become progressively more thermostable and chemically inert.

PHOTOLYSIS, PYROLYSIS AND $\text{S}_{\text{N}}1$ SUBSTITUTION

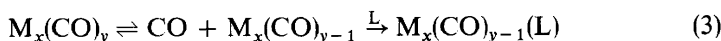
Photolysis, pyrolysis and $\text{S}_{\text{N}}1$ substitution can be considered together, because they all begin with transfer of electronic charge from the bonding frontier orbital. If the accepting antibonding orbital is mainly associated with the carbonyl groups, the process will transfer back some of the charge donated by the ligands and will usually be followed by breaking of a metal-carbon bond.

Photolysis needs a more involved technique, but this is compensated by the lower reaction temperature, a very important advantage for compounds which generally present low-to-moderate thermal stability. At present these processes are often used as synthetic methods, two typical examples being^{20, 21}:



The first reaction gives a tetrahedral cluster in which the four carbonyl groups are bonded to the four faces; in the second case a very interesting compound containing a linear sequence of three different metals results.

A general discussion of substitution processes in cluster carbonyl compounds is not possible owing to the paucity of information reported in the literature²²⁻²⁵; altogether there is indication of increasing $\text{S}_{\text{N}}1$ contribution on decreasing the basicity of the ligand^{23, 24}. The $\text{S}_{\text{N}}1$ reactions are analogous to photolysis and pyrolysis processes, but with them removal of a carbonyl group takes place in the presence of a different ligand and in the next recombination step there is competition between the carbon monoxide and the ligand:



Considering a typical reaction such as the reaction between tertiary phosphines and clusters $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) or $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) it is easily seen from the literature data⁶ that more energetic reaction

conditions are necessary as one passes down the subgroup. The iron, cobalt and rhodium compounds react with triphenylphosphine at room temperature, but the ruthenium, osmium and iridium ones require heating to 60°–140°. In all cases it has been possible to isolate substitution products, without breaking metal–metal bonds. For instance reaction between $\text{Rh}_4(\text{CO})_{12}$ and triphenylphosphine gives $\text{Rh}_4(\text{CO})_{11}(\text{PPh}_3)$, $\text{Rh}_4(\text{CO})_{10}(\text{PPh}_3)_2$ and $\text{Rh}_4(\text{CO})_9(\text{PPh}_3)_3$, breaking occurring only with a further excess of triphenylphosphine⁹.

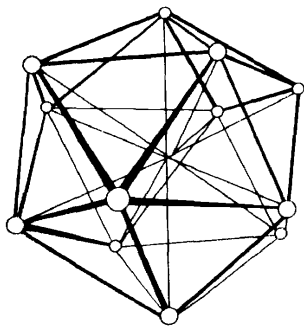
It is worth pointing out that the more reactive carbonyls have structures with bridging carbonyl groups, involving a higher back-donation from the metal atoms. The increased back-donation is shown by the stretching frequencies and the carbonyl distances reported in *Table 4*; the order of back-donation is terminal < edge bridging < face bridging⁶.

Table 4. Representative stretching frequencies and distances for different types of carbonyl groups⁶

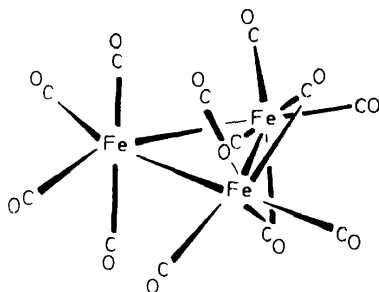
Type of carbonyl group	C=O distance, Å	$\nu_{(\text{C}=\text{O})}$, cm^{-1}
Terminal	1.12–1.19	2150–1950 (1750)*
Edge bridging	1.16–1.20	1900–1750 (1650)*
Face bridging	1.19–1.22	1800–1700 (1600)*

* Observed only in the presence of negative charges or of strong donor ligands.

It has been suggested⁷² that the structures of the $\text{M}_3(\text{CO})_{12}$ and $\text{M}_4(\text{CO})_{12}$ polynuclear carbonyls can be interpreted by considering the geometry of the oxygen atoms of the carbonyl groups. The less crowded eicosahedral structure of *Figure 1* is associated with bringing carbonyl groups [$\text{Fe}_3(\text{CO})_{12}$ ²⁶, $\text{Co}_4(\text{CO})_{12}$ ²⁷ and $\text{Rh}_4(\text{CO})_{12}$ ²⁸] and requires high back-donation from the metal atoms.



Eicosahedron



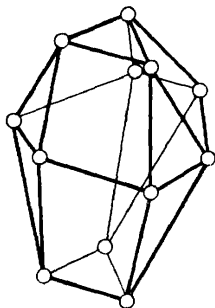
$\text{Fe}_3(\text{CO})_{12}$

Figure 1. (Reproduced in part from ref. 26)

The much more sterically crowded truncated bipyramid [*Figure 2*; $\text{Ru}_3(\text{CO})_{12}$ ²⁹ and $\text{Os}_3(\text{CO})_{12}$ ³⁰] and truncated tetrahedron [*Figure 3*; $\text{Ir}_4(\text{CO})_{12}$ ²⁸] without bridging carbonyl groups are preferred only for the more noble metals which are not prone to a high degree of back-donation.

It is therefore tempting to speculate that a low ionization potential of the metal will favour both a less strained structure with bridging carbonyl groups and formation of an intermediate $M_x(CO)_{11}$ in the S_N1 substitution.

The fate of the polynuclear derivative, when some carbonyl groups have been replaced by a tertiary phosphine and the electronic density and steric pressure have increased, can be explained qualitatively. When the metal-metal bonds are strong, or other bonds contribute to bridging between the metals, only formation of bridging carbonyl groups is expected, e.g. in $Ir_4(CO)_{10}(PPh_3)_2$ ³¹ and in $CH_3CCO_3(CO)_7(PPh_3)_2$ ³². Where the metal-metal bonds are weaker, as with cobalt and iron dodecacarbonyls, easy breaking of clusters is generally observed.



Truncated bipyramid

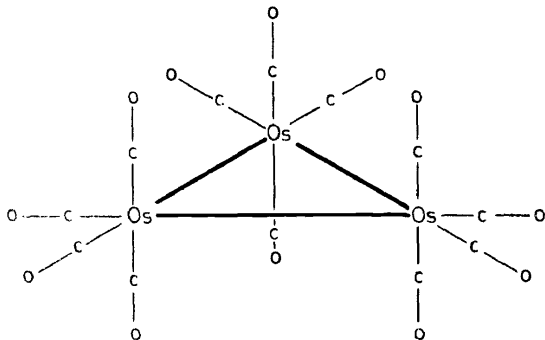
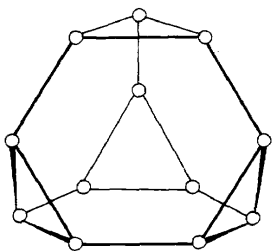
 $Os_3(CO)_{12}$

Figure 2.



Truncated tetrahedron

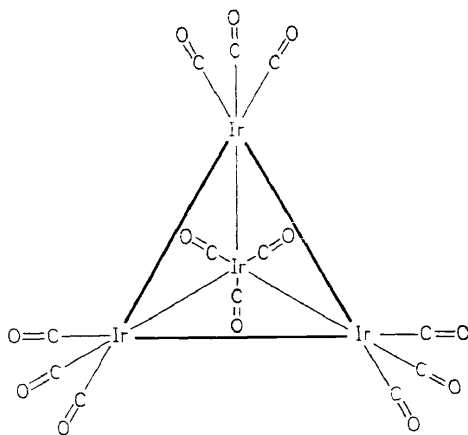
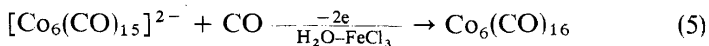
 $Ir_4(CO)_{12}$

Figure 3.

OXIDATION AND REACTION WITH ELECTROPHILIC REAGENTS

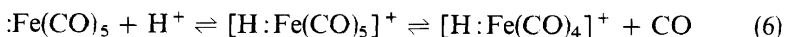
Increase in the oxidation state of metal atoms of a polynuclear metal carbonyl can generally be expected to give a less stable compound, because stability of carbonyl compounds is generally associated with low oxidation states. Oxidation reactions have only very seldom been of significant synthetic value. A case in point is oxidation of a polynuclear carbonyl-metallate to the corresponding polynuclear carbonyl which has been used to obtain hexanuclear $\text{Co}_6(\text{CO})_{16}$; this must be effected in a medium in which only the carbonylmetallate is soluble³³, otherwise there is complete decomposition³⁴



Another similar example is the synthesis³⁵ of $\text{Fe}_3(\text{CO})_{12}$ from $[\text{Fe}(\text{CO})_4]^{2-}$ and MnO_2 .

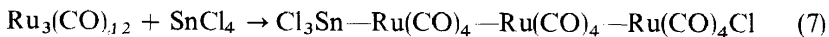
Sometimes, when metal-metal bonds are very strong, it is possible to obtain compounds resulting from partial oxidation of zerovalent starting derivatives. This applies in the reaction between $\text{Os}_3(\text{CO})_{12}$ and halogens, which give linear clusters³⁶ of the type $\text{X}-\text{Os}(\text{CO})_4-\text{Os}(\text{CO})_4-\text{Os}(\text{CO})_4\text{X}$; but with the corresponding iron and ruthenium derivatives there is complete break-up of the cluster structure³⁷. Kinetic study of this reaction indicates initial formation of a Lewis complex³⁸ $\text{Os}_3(\text{CO})_{12} \cdot \text{X}_2$.

The formation of such acid-base complexes corresponds to extraction of electrons from the bonding frontier orbitals, and represents a general method for activating metal carbonyls, as is well known in connection with labilization³⁹ of the carbonyl groups in $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4(\text{PPh}_3)$. The lowering of electronic density at the metal centre is reflected in less back-donation from metal to carbon monoxide, and hence in less bonding energy and increased lability. A half-life time of about four years for the exchange of iron pentacarbonyl with ^{14}C O is reduced to few minutes by trifluoroacetic acid³⁹



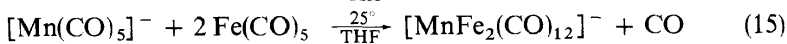
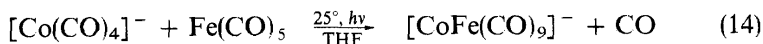
Analogous protonated compounds have been obtained recently from $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ in concentrated sulphuric acid and have been isolated as stable hexafluorophosphate salts⁴⁰ $[\text{HRu}_3(\text{CO})_{12}] [\text{PF}_6]$ and $[\text{HOs}_3(\text{CO})_{12}] [\text{PF}_6]$.

A similar activation by aluminium bromide, through formation of the complex $\text{Co}_2(\text{CO})_8 \cdot \text{AlBr}_3$, is responsible for the synthesis⁴¹ of derivatives of the cation $[\text{Co}_3(\text{C}_6\text{H}_6)_3(\text{CO})_2]^+$ starting from $\text{Co}_2(\text{CO})_8$, benzene and AlBr_3 . Moreover the complicated insertion reaction of tin(IV) halides in metal-metal bonds has been shown to proceed⁴² through a similar Lewis complex with $\text{Ru}_3(\text{CO})_{12}$:



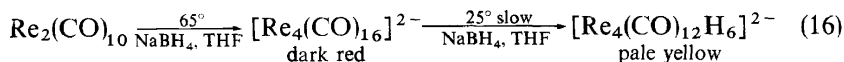
It seems probable therefore that electrophilic activation of polynuclear metal carbonyls will be increasingly used in the next few years.

CHEMISTRY OF POLYNUCLEAR METAL CARBONYL COMPOUNDS



It is now clear that a reduction process can be complicated by nucleophilic reduction from intermediate carbonylmetallates, and that the result can be highly dependent on minor variations such as order of mixing of the reagents. Another important effect arises from the presence of carbon monoxide as will be seen in the next section.

Sodium borohydride is another useful reducing agent, but unfortunately little is known of the mechanism of the reaction. Reduction of $\text{Re}_2(\text{CO})_{10}$ has been studied by Kaesz and co-workers^{49, 50}, who found reduction to the anion $[\text{Re}_4(\text{CO})_{16}]^{2-}$ to be followed by slow replacement of carbonyl groups by hydrogen atoms:

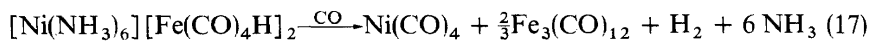


The possible formation of hydrido compounds should be carefully considered not only when using this reagent, but also when water is present and carbonylmetallates can be hydrolysed, as is well known for instance in the facile conversion³⁵ of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ to $[\text{Fe}_3(\text{CO})_{11}\text{H}]^-$.

Table 5. Comparison between nucleophilic and reducing power of carbonylmetallates⁴⁴

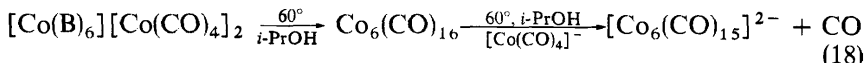
Carbonylmetallate	Relative rate for nucleophilic substitution	Half polarographic wave $-E_{\frac{1}{2}}$ (oxidn, Pt)
$[(\pi\text{-Cp})\text{Fe}(\text{CO})_2]^-$	7×10^7	1.6
$[(\pi\text{-Cp})\text{Ru}(\text{CO})_2]^-$	7×10^6	1.5
$[(\pi\text{-Cp})\text{Ni}(\text{CO})]^-$	5.5×10^6	1.4
$[\text{Re}(\text{CO})_5]^-$	2.5×10^4	0.9
$[(\pi\text{-Cp})\text{W}(\text{CO})_3]^-$	5×10^2	1.0
$[\text{Mn}(\text{CO})_5]^-$	77	0.55
$[(\pi\text{-Cp})\text{Mo}(\text{CO})_3]^-$	67	0.55
$[(\pi\text{-Cp})\text{Cr}(\text{CO})_3]^-$	4	0.8
$[\text{Co}(\text{CO})_4]^-$	1	0.2
$[\text{Cr}(\text{CO})_5(\text{CN})]^-$	0.01	-0.2
$[\text{Mo}(\text{CO})_5(\text{CN})]^-$	0.01	-0.2
$[\text{W}(\text{CO})_5(\text{CN})]^-$	0.01	-0.2

A particular type of reduction is possible when the carbonylmetallate is bonded to a transition metal cation. In this case reaction can more correctly be regarded as electron redistribution, because there is simultaneous cation reduction and anion oxidation. The first example of this reaction was discovered by Hieber in 1936⁵¹

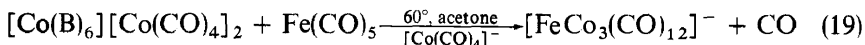


Only later was this reaction used for synthetic purposes, e.g. the case of the anion $[\text{Co}_6(\text{CO})_{15}]^{2-}$. The first step in this synthesis is believed to involve formation of the intermediate $\text{Co}_3(\text{CO})_8$ by electron redistribution in a cobalt(II)

carbonylcobaltate $[\text{Co}(\text{B})_6][\text{Co}(\text{CO})_4]_2$, a reaction which occurs with particular ease when B is a weak Lewis base with high steric requirements (such as acetone or isopropanol). This step will be followed by condensation to $\text{Co}_6(\text{CO})_{16}$ and reduction⁵²:



This mechanism is in accord with the synthesis⁵³ of the anion $[\text{Ni}_2\text{Co}_4(\text{CO})_{14}]^{2-}$ from $[\text{Ni}(\text{B})_6][\text{Co}(\text{CO})_4]_2$. The intermediate $\text{Co}_3(\text{CO})_8$ can also condense^{53, 54} with $\text{Co}_2(\text{CO})_8$ to give $\text{Co}_4(\text{CO})_{12}$; or with $\text{Fe}(\text{CO})_5$ to give, after reduction, the anion $[\text{FeCo}_3(\text{CO})_{12}]^-$

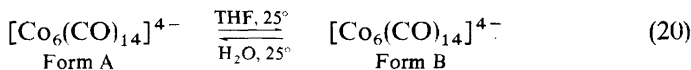


The scope of this reaction seems to be broad, owing to many possible variations in transition metal cation and carbonylmetallate.

NUCLEOPHILIC ATTACK

Nucleophilic attack differs somewhat from reduction, though in both cases the first step formally involves electron addition at the frontier antibonding orbital. This orbital is probably of predominantly carbon monoxide character, and a fractional positive charge is present on the carbonyl carbon atoms favouring attack at those particular positions. The presence of a positive charge is shown by the dipole moment of the $\text{M}=\text{C}=\text{O}$ group, which is generally of about 0.8 D and is directed toward the metal. This fractional positive charge at the carbonyl carbons arises from difference in donation and back-donation, and owing to greater back-donation to the bridging carbonyl groups, the latter are expected to react less easily than the terminal ones. Generally these reactions can be readily explained by assuming a direct nucleophilic attack at a carbonyl group, and here we found again a strict similarity with organic chemistry.

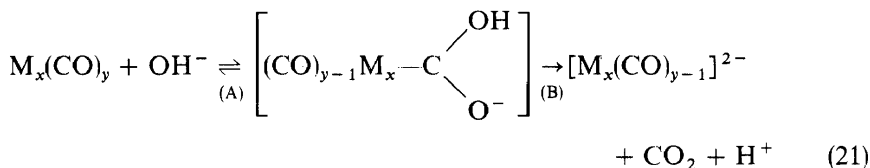
A first type of nucleophilic attack at carbonyl carbon can take place through a pair of electrons on a neighbouring metal atom. This kind of mechanism is consistent both with migration of carbon monoxide in different positions of a cluster, and over a metallic surface. Examples of this behaviour in binuclear compounds are well known, e.g. with $\text{Co}_2(\text{CO})_8$ ^{55, 56} and $(\pi\text{-Cp})_2\text{M}_2(\text{CO})_4$ ($\text{M} = \text{Fe}, \text{Ru}$)^{57, 58}. Recently this migration has been also observed in polynuclear derivatives, such as the $[\text{Co}_6(\text{CO})_{14}]^{4-}$ anion⁴⁵ and $\text{CH}_3\text{CCO}_3(\text{CO})_7(\text{PPh}_3)_2$ ³². The easy isomerization has led to considerable experimental difficulty in isolating derivatives of the $[\text{Co}_6(\text{CO})_{14}]^{4-}$ anion, whose structure is apparently greatly dependent on the extent of dissociation of the corresponding salt⁴⁵



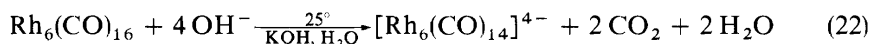
6 terminal and 8 face bridging carbonyl groups; $\nu_{\text{C=O}}$ at 1640–1680 cm^{-1} .	Structure unknown, probable occurrence of edge bridging carbonyl groups; $\nu_{\text{C=O}}$ at 1710–1760 cm^{-1} .
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Direct nucleophilic attack at carbonyl carbon by amines has been proved in several cases through isolation of the related carboxamide derivatives

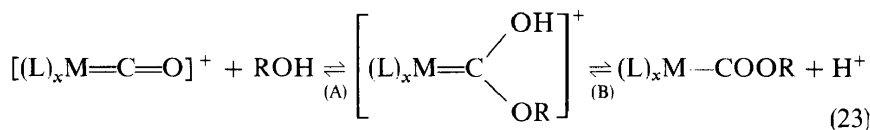
such as $R_2NCOC_0(CO)_3(PPh_3)^{59-62}$, and the same attack is probably involved in reactions of oxygen Lewis bases. Kruck originally suggested that reaction between carbonyls and alcoholic alkali follows a scheme of this type⁶³:



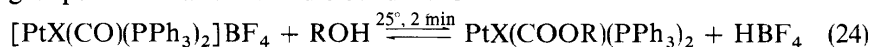
A simple reaction of this type for polynuclear metal carbonyls is⁹



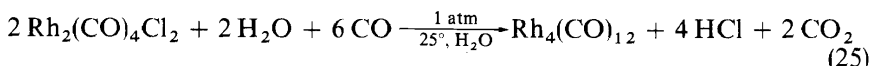
In some cases nucleophilic attack on the carbonyl group is ambiguous and it is difficult to discriminate between different nucleophilic agents such as water and OH^- ion, or alcohol and OR^- ion. The formation of carboalkoxy groups was originally explained by Malatesta as direct attack by the alcohol molecule⁶⁴:



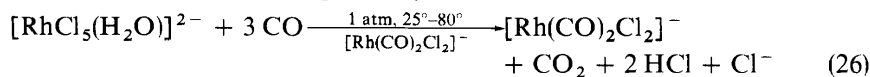
This mechanism agrees with the recent report of formation of carboalkoxy groups in methanol in acidic conditions⁶⁵



Both processes 21 and 23 can be divided into two reactions (A) and (B). Reaction (A) is a nucleophilic attack and will be expected to be favoured by a high oxidation state of the metal, back-donation from metal to carbon then being less and the fractional charge on carbon greater. Reaction (B) is the elimination of a proton, a process depending on ease of lowering the state of oxidation of the metal. Both effects are probably involved in the extraordinarily facile reduction of $Pt(CO)_2Cl_2$ and $Rh_2(CO)_4Cl_2$ by water under acidic conditions^{66, 67}. Under carbon monoxide in the case of rhodium the first reaction product is $Rh_4(CO)_{12}$, which easily passes⁶⁸ to the thermodynamically more stable $Rh_6(CO)_{16}$:



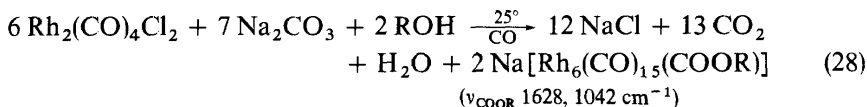
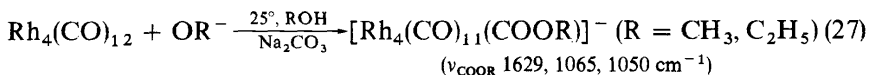
In acidulated water this process can be combined with autocatalytic reduction of rhodium (III) chloro complexes by carbon monoxide⁶⁹



We have recently obtained $Rh_4(CO)_{12}$ in about 90 per cent yield starting directly from sodium hexachlororhodate which is reduced to $[Rh(CO)_2Cl_2]^-$

anion using powdered copper metal and then converted¹² to $\text{Rh}_4(\text{CO})_{12}$ by buffering at about pH 4.

Reduction would be expected to be favoured by the possibility of distributing the negative charge over several metal atoms. This is probably the key factor in the formation¹² of carboalkoxy derivatives of the rhodium clusters:

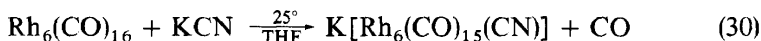


Formation of these carboalkoxy derivatives is reversible, $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ being regenerated by reaction with acids.

The stability of substituted Rh_6 clusters is confirmed by the reaction¹² of $\text{Rh}_4(\text{CO})_{12}$ with tetraalkylammonium iodides

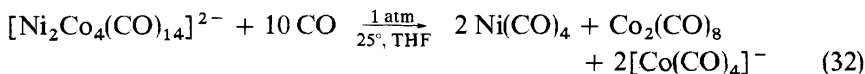
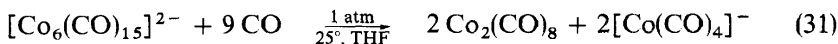


and by the reaction¹² of $\text{Rh}_6(\text{CO})_{16}$ with potassium cyanide

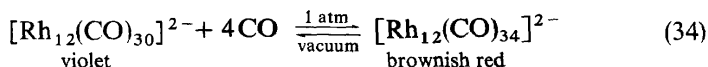
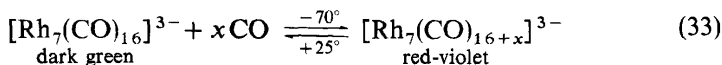


Preliminary x-ray results⁷⁰ show that in this type of derivative there is only substitution of a terminal carbonyl group of $\text{Rh}_6(\text{CO})_{16}$; infra-red spectra of the species $[\text{Rh}_6(\text{CO})_{15}(\text{R})]^-$ ($\text{R} = \text{COOR}$, I , CN , CONR_2 and COCF_3) are all very similar. We can reasonably expect a chemistry of substituted clusters analogous to the well known chemistry of substituted simple metal carbonyls, which can be of particular significance for some still obscure aspects of the hydroformylation process.

Carbon monoxide itself can participate in a peculiar type of nucleophilic attack in which considerable possible electrophilic assistance through back-donation imparts to carbon monoxide an ambiguous character. Usually these reactions involve metal-metal bond breaking^{52, 53}:



Sometimes these reactions are reversible¹²:



($\nu_{\text{C=O}}$ 2053s, 2040s, 1771s cm^{-1}) ($\nu_{\text{C=O}}$ 2055s, 2010s, 1868m, 1838m, 1785m cm^{-1})

Possibly with the Rh_{12} cluster there is a change from octahedra to tetrahedron chains of rhodium atoms in agreement with observed preservation of diamagnetism.

CONCLUSIONS

Consideration of the limited information at present available regarding reactivity of polynuclear metal carbonyls enables the following general conclusions to be drawn:

1. The polynuclear metal carbonyls become progressively more thermostable and chemically inert on passing down a subgroup, while at the same time the metal-metal bond strength increases.
2. Polynuclear carbonyls react readily with electrophilic agents with considerable weakening of metal-carbon bonds. Evidence for attack at the oxygen atoms of the carbonyl group is lacking^{7,1}.
3. Polynuclear metal carbonyls are readily reduced by several strong reducing agents, in agreement with the presence of delocalized low-energy orbitals and reminiscent of aromatic organic compounds.
4. Nucleophilic attack on the carbon atoms of the carbonyl groups takes place readily, suggesting the presence of a positive fractional charge analogous to that observed with organic carbonyl compounds.

ACKNOWLEDGEMENTS

I am indebted to my colleagues at the Institute of General and Inorganic Chemistry at Milan University for many patient discussions, to Prof. L. Malatesta for his continuous encouragement, to Dr S. Martinengo for his collaboration and to Dr V. Albano for several structure determinations. I would also like to mention the following students who have contributed experimentally to our work in this field: Dr G. Tagliaferri (1966), Dr G. Longoni (1967), Dr A. Quarta (1967), Dr A. Cavalieri (1968), Dr R. Bravi (1968), Dr A. Viviani (1969), Dr A. Ferrero (1969) and Sig. G. Giordano (1969). I thank the CNR for financial assistance.

REFERENCES

- ¹ F. A. Cotton, *Quart. Rev. Chem. Soc. Lond.* **20**, 389 (1966).
- ² F. A. Cotton, *Rev. Pure Appl. Chem. (Australia)*, **17**, 25 (1967).
- ³ J. Lewis, *Pure Appl. Chem.* **10**, 11 (1965).
- ⁴ B. Penfold, *Perspectives in Structural Chemistry*, **2**, 71 (1968).
- ⁵ D. L. Kepert and K. Vrieze, *Halogen Chemistry*, **3**, 1 (1967).
- ⁶ P. Chini, *Inorg. Chim. Acta Rev.* **2**, 31 (1968).
- ⁷ M. C. Baird, *Progr. Inorg. Chem.* **9**, 1 (1968).
- ⁸ W. Heiber and H. Beutner, *Z. Naturforsch.* **17b**, 211 (1962).
W. Heiber and E. H. Schubert, *Z. Anorg. Allg. Chem.* **338**, 32 (1965).
- ⁹ P. Chini and S. Martinengo, *Chem. Commun.* 1092 (1969).
- ¹⁰ H. Vahrenkamp, V. A. Uchtman and L. F. Dahl, *J. Am. Chem. Soc.* **90**, 3727 (1968).
- ¹¹ D. B. Yawney and F. G. A. Stone, *J. Chem. Soc. A*, 502 (1969).
- ¹² F. Cariati, P. Chini and S. Martinengo, unpublished results.
- ¹³ E. S. R. Gopal, *Specific Heat at Low Temperatures*. Heywood: London (1966).
- ¹⁴ K. A. Gscheidner, *Solid State Physics*, **16**, 275 (1964).
- ¹⁵ J. S. Griffith, *J. Inorg. Nucl. Chem.* **3**, 15 (1956).

- ¹⁶ B. F. Johnson, J. Lewis, I. G. Williams and J. M. Wilson, *J. Chem. Soc. A*, 341 (1967).
M. I. Bruce, *Advanc. Organometal. Chem.* **6**, 273 (1968).
- ¹⁷ Tables of interatomic distances, *Spec. Publ. No. 18*. The Chemical Society: London (1965).
- ¹⁸ *Handbook of Chemistry and Physics*, 46th ed. Chemical Rubber Publ. Co.: Cleveland, Ohio (1965-66).
- ¹⁹ A. F. Wells, *Structural Inorganic Chemistry*, 3rd ed., p 979. Oxford University Press: London (1962).
- ²⁰ R. B. King, *Inorg. Chem.* **5**, 2227 (1966).
- ²¹ G. O. Evans and R. K. Sheline, *J. Inorg. Nucl. Chem.* **30**, 2862 (1968).
- ²² G. Cetini, R. Ercoli, O. Gambino and G. Vaglio, *Atti Accad. Sci. Torino*, **99**, 1 (1965).
- ²³ G. Cetini, P. L. Stanghellini, R. Rossetti and O. Gambino, *Inorg. Chim. Acta*, **2**, 433 (1968).
- ²⁴ J. P. Candlin and A. C. Shortland, *J. Organometal. Chem.* **16**, 289 (1969).
- ²⁵ G. Cetini, O. Gambino, E. Sappa and G. Vaglio, *Ric. Sci.* **37**, 430 (1967) and *Atti Acad. Sci. Torino*, **101**, 855 (1966-1967).
- ²⁶ C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.* **91**, 1351 (1969).
- ²⁷ C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.* **88**, 1821 (1966).
- ²⁸ C. H. Wei, G. R. Wilkes and L. F. Dahl, *J. Am. Chem. Soc.* **89**, 4792 (1967).
- ²⁹ E. R. Corey and L. F. Dahl, *J. Am. Chem. Soc.* **83**, 2203 (1961).
R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).
- ³⁰ E. R. Corey and L. F. Dahl, *Inorg. Chem.* **1**, 521 (1962).
- ³¹ V. Albano, P. L. Bellon and V. Scatturin, *Chem. Commun.* 730 (1967).
- ³² B. H. Robinson and W. S. Tham, *J. Organometal. Chem.* **16**, P45 (1969).
- ³³ P. Chini, *Inorg. Chem.* **8**, 1206 (1969).
- ³⁴ M. Heintzeler and N. Kutepow, *Germ. Pat. No. 953 753* (6/10/55).
- ³⁵ W. Hieber and G. Brendel, *Z. Anorg. Allg. Chem.* **289**, 324 (1957).
- ³⁶ B. F. Johnson, J. Lewis and P. A. Kilty, *J. Chem. Soc. A*, 2859 (1968).
- ³⁷ W. Hieber and G. Bader, *Z. Anorg. Allg. Chem.* **201**, 329 (1931).
B. F. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc. A*, 792 (1969).
- ³⁸ J. P. Candlin and J. P. Cooper, *J. Organometal. Chem.* **15**, 230 (1968).
- ³⁹ F. Basolo and R. A. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., pp 545-546. Wiley: New York (1967).
- ⁴⁰ J. Knight and M. J. Mays, *Chem. Commun.* 384 (1969).
A. J. Deeming, B. F. Johnson and J. Lewis, *J. Organometal. Chem.* **17**, P40 (1969).
- ⁴¹ P. Chini and R. Ercoli, *Gazz. Chim. Ital.* **88**, 1170 (1958).
- ⁴² R. K. Pomeroy, M. Elder, D. Hall and W. A. G. Graham, *Chem. Commun.* 381 (1969).
- ⁴³ (a) E. Dessy, A. Kormann, C. Smith and R. Haytor, *J. Am. Chem. Soc.* **90**, 2001 (1968).
(b) E. De Boer, *Advanc. Organometal. Chem.* **2**, 115 (1964).
- ⁴⁴ R. E. Dessy, R. L. Pohl and R. B. King, *J. Am. Chem. Soc.* **88**, 5121 (1966).
- ⁴⁵ P. Chini, V. Albano and S. Martinengo, *J. Organometal. Chem.* **16**, 471 (1969).
- ⁴⁶ V. Anders and W. A. G. Graham, *J. Am. Chem. Soc.* **89**, 539 (1967).
- ⁴⁷ J. K. Ruff, *Inorg. Chem.* **7**, 1818 (1968).
- ⁴⁸ V. Anders and W. A. G. Graham, *Chem. Commun.* 291 (1967).
- ⁴⁹ R. Bau, B. Fontal, H. D. Kaesz and M. R. Churchill, *J. Am. Chem. Soc.* **89**, 6375 (1967).
- ⁵⁰ H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley and M. R. Churchill, *J. Am. Chem. Soc.* **91**, 1021 (1969).
- ⁵¹ W. Hieber, *Angew. Chem.* **49**, 463 (1936).
- ⁵² P. Chini and V. Albano, *J. Organometal. Chem.* **15**, 433 (1968).
- ⁵³ P. Chini, S. Martinengo and V. Albano, Proceedings of the International Symposium on Metal Carbonyls, paper A-3. *Inorg. Chim. Acta Ed.*: Venice, (2-4 September 1968).
- ⁵⁴ P. Chini, L. Colli and M. Peraldo, *Gazz. Chim. Ital.* **90**, 1005 (1960).
- ⁵⁵ K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).
- ⁵⁶ G. Bor, *Spectrochim. Acta*, **19**, 2065 (1963).
- ⁵⁷ K. Noack, *J. Organometal. Chem.* **7**, 135 (1967).
- ⁵⁸ F. A. Cotton and G. A. Yagupsky, *Inorg. Chem.* **6**, 15 (1967).
- ⁵⁹ W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer and N. Koizumi, *J. Am. Chem. Soc.* **87**, 3080 (1965).
- ⁶⁰ R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta*, **2**, 3 (1968).
- ⁶¹ L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968).
- ⁶² J. Palagyi and L. Marko, *J. Organometal. Chem.* **17**, 453 (1969).
- ⁶³ T. Kruck, M. Hofler and M. Noack, *Chem. Ber.* **99**, 1153 (1966).

- ⁶⁴ L. Malatesta, G. Caglio and M. Angoletta, *J. Chem. Soc.* 6974 (1965).
- ⁶⁵ H. C. Clark, K. R. Dixon and W. J. Jacobs, *J. Am. Chem. Soc.* **91**, 1346 (1969).
- ⁶⁶ G. Booth, J. Chatt and P. Chini, *Chem. Commun.* 639 (1965).
- ⁶⁷ P. Chini and S. Martinengo, *Chem. Commun.* 251 (1968).
- ⁶⁸ P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 21 (1969).
- ⁶⁹ B. R. James and G. L. Rampel, *J. Chem. Soc. A*, 78 (1969).
- ⁷⁰ V. Albano, personal communication.
- ⁷¹ Note added in proof: Adducts of this kind have recently been obtained by N. J. Nelson, D. F. Shriver and N. E. Kime, *Progress in Organometallic Chemistry* (edited by M. I. Bruce and F. G. A. Stone), paper U-2. The Chemical Society: London (1969).
- ⁷² P. Corradini and G. Paiaro, *Ric. Sci.* **36**, 365 (1966).