

# Platinum Metal Cluster Carbonyls and Their Metal Surface Analogues

## A METAL PHYSICS FRAMEWORK FOR CLUSTER CHEMISTRY

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*This article describes some of the experimental evidence that suggests a useful analogy can be made between the transition metal cluster carbonyls and the corresponding carbon monoxide-metal chemisorption systems. This analogy is interpreted using recent electronic structure results in metal physics, leading to a theoretical framework in which cluster chemistry can be approached.*

In recent years numerous metal cluster compounds, in which metal atoms are part of a chemically bonded metal-metal network, have been prepared and characterised. The binary transition metal cluster carbonyls, which I define as species with generic formula  $M_m(\text{CO})_n^Q$ ,  $m \geq 4$ ,  $n \approx 3m$ ,  $Q \geq 0$ , constitute a large and important family of such molecules. As a recent review in this Journal testifies (1), there is currently much interest in these unusual cluster compounds because of their intermediate position between monometal coordination compounds and the chemisorption of simple molecules on metal surfaces. The investigation of their physical and chemical properties is being actively pursued both for academic reasons and because of its relevance to the study of surface reactions for use in catalytic and other industrial processes. In this

review I will describe some of the evidence that suggests that cluster carbonyls are much more like their metal surface analogues than the simple mononuclear transition metal carbonyls, and attempt to summarise some of the theoretical ideas that seem to be useful in this unexpected situation which, as we shall see, is peculiar to the platinum metal group.

### Systematics

Whereas mononuclear and/or binuclear binary carbonyls are formed with most of the elements of the transition metal block, the formation of stable, stoichiometric cluster carbonyls (tetranuclear species or larger) appears to be confined almost exclusively to the Group VIII metals (2) with the exception of palladium—see Table I.

Palladium is evidently a borderline case, for phosphine substituted carbonyl cluster species like  $\text{Pd}_3(\text{CO})_3\text{PPh}_3$  have been characterised, and since gold is known to form stable phosphine cluster cations such as  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$ , it appears that palladium resembles gold rather more than the other platinum metals.

Part of the experimental basis for the metal cluster-metal surface analogy can be found in the systematics of carbon monoxide chemisorption on transition metal surfaces. Chemisorption of the first-row diatomic molecules on

VIII			IB
Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

Table II							
Systematics of Carbon Monoxide Chemisorption on Transition Metal Surfaces							
IV	V	VI	VII	VIII			IB
Ti D	V	Cr	Mn	Fe D/A	Co A	Ni A	Cu A
Zr	Nb D	Mo D	Tc	Ru A	Rh A	Pd A	Ag A
Hf	Ta D	W D/A	Re D/A	Os A	Ir A	Pt A	Au A

D = dissociative adsorption     $\text{CO} \rightarrow \text{C}^* + \text{O}^*$                       A = associative adsorption     $\text{CO} \rightarrow \text{CO}^*$

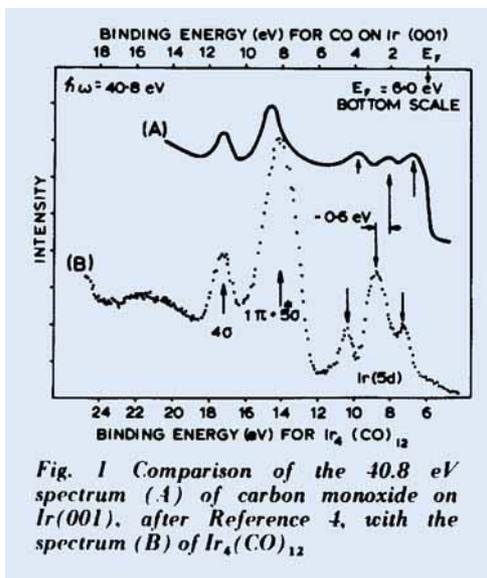
transition metal surfaces has been extensively studied with a variety of physical measurement techniques (low energy electron diffraction, photoemission, vibrational spectroscopy using infra-red radiation and the electron energy loss technique), and we can now confidently describe the systematics of adsorbate bonding in relation to the Periodic Table (3). At low coverage one finds that chemisorption can take place either through dissociative adsorption (D), involving rupture of the molecular bond, or by associative adsorption (A), in which the diatomic molecule largely preserves its identity as a ligand. An obvious parameter to use to correlate the behaviour of different diatomic molecules is the energy required to rupture the molecular bond—the diatomic dissociation energy  $E_b$ . Experimentally one finds that a definite dividing line between dissociative/associative adsorption moves steadily to the right across the Periodic Table as the energy  $E_b$  decreases. The systematics for chemisorbed carbon monoxide, with  $E_b = 11.1$  eV, are summarised in Table II.

When we note that chemisorbed diatomic species on the noble metals (IB) have very low binding energies, a comparison of Tables I and II reveals a striking correlation between metal cluster carbonyl formation and associative chemisorption of carbon monoxide on the corresponding metal surfaces at low coverage that is centred on the Group VIII metals.

Further evidence to support the belief that metal cluster carbonyls are related to chemisorbed carbon monoxide on metal surfaces can be

found in recent photoemission studies. Recall that in the UPS photoemission experiment photons with ultra-violet energy are incident on the sample which is ionised, and the kinetic energy of the emitted electrons is monitored to give a spectrum that can be related to the valence electronic structure of the compound under investigation. It appears that transition metal carbonyls with more than about three transition metal atoms have photoemission spectra that correspond very well with the photoemission spectra of carbon monoxide chemisorbed on the surface of the bulk metal: such comparisons have been made for  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Ir}_4(\text{CO})_{12}$  (4) and  $\text{Os}_6(\text{CO})_{18}$  (5).

These spectra all show the same general features, shown in Figure 1, which have been assigned to definite aspects of the electronic structure: in both carbonyls and chemisorbed carbon monoxide systems, ionisation begins with transitions out of the metal "d-band" which typically for clusters extends 3 to 4 eV below the ionisation threshold. Then below the metal d-band and separated from it by  $\geq 1$  eV is a large peak that is assigned to the carbonyl "1 $\pi$ " and "5 $\sigma$ " molecular orbitals which are not differentiated: this peak is typically 2 to 3 eV wide, and below it is a smaller peak that is assigned to the carbonyl "4 $\sigma$ " levels. It is to be noted, however, that the cluster-surface analogy has to be handled carefully: the work function  $\phi$  of a transition metal surface with a monolayer of carbon monoxide is increased by  $\lesssim 3/4$  eV as compared with the clean metal surface for



which  $\phi$  is typically  $\approx 5$  eV (6). On the other hand, the ionisation potentials of cluster carbonyls in the gas phase are several volts larger, for example, the ionisation threshold for  $\text{Os}_6(\text{CO})_{18}$  is  $\approx 8$  eV, and this significant shift in a bulk property is largely due to intermolecular electronic and nuclear relaxation effects that are possible only in the condensed phase.

One other piece of physical information that is pertinent here lies in the structural data of molecular geometries. As might be guessed from their name, transition metal cluster carbonyls can be visualised as consisting of an interior polyhedron of metal atoms with metal-metal nearest-neighbour distances comparable to (usually a little longer) those found in the bulk metal (2, 7), surrounded by an approximately spherical shell of carbonyl groups bonded to the metal cluster through the carbon atom. The carbonyl ligands may be bonded to vertices, edges or faces of the metal polyhedron with metal-carbon bond distances closely similar to those found with chemisorbed carbon monoxide on metal surfaces. At relatively low temperatures in solution,  $^{13}\text{C}$  NMR spectroscopy shows that the carbonyl groups in many cluster carbonyls are mobile over part or all of the metal cluster: evidently

the ligands have little preference as to their bonding sites on the metal polyhedron and one only expects definite cluster structures in the solid phase.

## Interpretation

Taken together the experimental information reviewed here suggests that the intuitively appealing physical picture of a small metal particle encased in a sheath of insulating material (a monolayer of carbon monoxide) provides a useful framework for a discussion of the physical properties of transition metal cluster carbonyls. The catch, if it is a catch, is that this model need not require a close correspondence between the chemical reactivity of metal cluster carbonyls, and the corresponding transition metal surfaces on which carbon monoxide has been chemisorbed since chemical reactivity is often closely controlled by rather small energy terms. All is not lost, however, for we have abundant experience in chemistry that semi-empirical theories of chemical reactivity based on arguments like frontier orbital theory, the Woodward-Hoffmann rules and so on, can be extremely useful in rationalising the course of known reactions and predicting the outcome of novel chemical situations. These methods can be expected to be successful when we have a pretty good idea of the overall features of the electronic structure of the participating molecules. Thus, to gain insight into the chemical reactivity of metal cluster carbonyl species, and even the wider topic of metal particles generally, a necessary pre-requisite is to understand the electronic structure of these systems.

The above comparison of metal cluster carbonyls with carbon monoxide-transition metal chemisorption systems strongly suggests that the local electronic environment of a transition metal atom in a metal cluster carbonyl cannot be very different from that of a metal atom at a metal surface or even in the bulk metal, and that the major differences should be accounted for by the differences in co-ordination number, and by the presence of the dielectric layer (the carbonyl ligands).

**The theoretical interpretation of the metal cluster–metal surface analogy I have described is thus that the local electronic state of a transition metal atom in a cluster carbonyl is much closer to that found in bulk metal than to the isolated metal atom or isolated metal atom plus a few carbonyl ligands (the mononuclear carbonyl complexes).**

This view is consistent with all the experimental information I know of, and has the pleasing feature that it suggests a very profitable insight into this burgeoning area of organometallic chemistry may be gained from an acquaintance with the facts of the modern electronic theory of bulk transition metals (7).

This is not the place to enter into a detailed discussion of the theory of transition metals which is so recent (8) as not to have reached textbooks of either solid-state physics or inorganic chemistry. It is important to realise, however, that the bulk transition metals can now be described in a **simple and transparent molecular orbital framework** that gives quantitative results for properties like the cohesive energy per atom (related to the bond energy), the bulk modulus and compressibility, metallic radii and the structural systematics (f.c.c./b.c.c./h.c.p.) across the Periodic Table (8). There are two distinct features in the electronic structure of these metals. First, the energy bands formed from the valence s- and p-atomic orbitals are similar to those found in the simple metals and are associated with quantum states in which the electrons move through the whole crystal as though they were almost free particles in a large box. Second, and of crucial significance here, there are electron states localised about atomic centres that are formed from the valence atomic d-orbitals and are describable in the linear combination of atomic orbitals (L.C.A.O.) framework familiar in quantum chemistry. It turns out that in transition metal structures at or near the equilibrium volume, the d-electrons lead to a strongly attractive force between adjacent metal atoms, whereas the valence s- and p-electrons lead to a repulsive interaction between the atoms, because the

s-, p-electrons are repelled from the metal ion cores. The equilibrium structure arises from the competition between these two opposing effects. On the other hand the cohesive energy is almost completely determined by the d-electron interactions, and in the L.C.A.O. framework referred to above can be expressed in terms of the co-ordination number ( $Z$ ) of a metal atom, and the nearest-neighbour distance  $R$ ,

$$U \approx \frac{A_d \sqrt{Z}}{R^5} \quad (i)$$

$A_d$  is a constant determined by the atomic potential of the given metal, and the number of d-electrons. A full analysis shows that  $U$  is simply proportional to the root mean square width of the d-band in the metal,  $\overline{W}_d$ , and this is the origin of the  $\sqrt{Z}$  dependence (7).

How can we use this information in the context of metal cluster molecules? It is obvious that the free-electron-like sp-bands in the metal will be markedly affected by chemical bonding with the ligands: on the other hand, the d-electron interactions between the metal atoms are sufficiently localised that in a first approximation we can expect a formula like equation (i) still to hold. Moreover we should still expect the equilibrium structure of the metal cluster to reflect the competition between attractive d-electron interactions, which should follow much the same law as in the bulk metal, that is equation (i), and repulsive s,p-electron interactions which will be a sensitive function of the donor/acceptor properties of the ligands. As an example, the usual picture of bonding in metal carbonyls has the carbonyl lone-pair (the  $5\sigma$  m.o.) **donating** electrons to the metal cluster: most cluster carbonyls have structures in which the metal unit is completely enclosed by a nearly spherical shell of carbonyls and so we expect the s,p-electron density about each metal atom to be increased compared with the situation in the bulk metal. The fact that metal clusters in metal cluster carbonyls are expanded in comparison with the structural units in the bulk metals (2) should not then be a surprise. Note also that molecules like  $\text{Pt}_3(\text{CO})_6^-$  which have planar ( $D_{3h}$ ) structures have metal–metal

bonds that are shorter than in the bulk because there are no ligands squeezing in the s,p-electrons above and below the molecular plane (7).

When we look at the parameters describing the electronic structure of the bulk platinum metals we notice that palladium has a much narrower d-band than the other platinum metals, and hence the palladium–palladium bond energy is likely to be small in palladium clusters: further, the highest occupied level (the Fermi level) in palladium is more than 1 eV lower than in platinum. The electronic structure of bulk palladium is thus much more like gold than the other Group VIII metals, and this is the clue to the rationalisation of the anomalous behaviour of palladium (7).

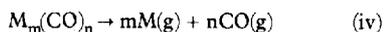
Finally, equation (i) can also give us a framework for the thermochemistry of metal cluster carbonyls. Suppose we adopt equation (i) for the cohesive energy of the metal cluster in a metal cluster carbonyl, arguing that since d-electrons are highly localised, the constant  $A_d$  will not be changed too much in going from the bulk metal to the molecule. We can then use equation (i) to write a cohesive energy per atom for the cluster atoms as:

$$U^{\text{cluster}} \approx \left( \frac{R^{\text{bulk}}}{R^{\text{cluster}}} \right)^5 \cdot \left( \frac{Z^{\text{cluster}}}{Z^{\text{bulk}}} \right)^{\frac{1}{2}} \cdot U^{\text{bulk}} \quad (\text{ii})$$

or in terms of bond-energies  $b$  ( $b = 2U/Z$ ):

$$b^{\text{cluster}} \approx \left( \frac{R^{\text{bulk}}}{R^{\text{cluster}}} \right)^5 \cdot \left( \frac{Z^{\text{bulk}}}{Z^{\text{cluster}}} \right)^{\frac{1}{2}} \cdot b^{\text{bulk}} \quad (\text{iii})$$

If  $\Delta H_{\text{disrupt}}$  is the enthalpy of disruption for the metal cluster carbonyl, that is, the enthalpy for the process,



and  $D(M-\text{CO})$ , the metal-carbonyl bond-energy, we have,

$$nD(M-\text{CO}) = \Delta H_{\text{disrupt}} + mU^{\text{cluster}} \quad (\text{v})$$

In bulk rhodium metal (f.c.c.) we have  $Z^{\text{bulk}} = 12$ , and  $R^{\text{bulk}} = 2.69\text{\AA}$ : in the tetrahedral cluster  $\text{Rh}_4(\text{CO})_{12}$  we have  $Z = 3$ ,  $R = 2.73\text{\AA}$ , and in octahedral  $\text{Rh}_6(\text{CO})_{16}$  we have  $Z = 4$ ,  $R = 2.78\text{\AA}$ . Finally the value of  $\Delta H_{\text{disrupt}}$  for  $\text{Rh}_4(\text{CO})_{12} = 2,648\text{kJ/mol}$ , and

for  $\text{Rh}_6(\text{CO})_{16} = 3,874\text{kJ/mol}$ . The cohesive energy in bulk rhodium is  $-5.78\text{ eV/atom}$ , corresponding to  $b^{\text{bulk}} = 93\text{ kJ/mol}$  (9). Using these values and equation (ii) we calculate:

$$U^{\text{oct}} = 0.49 U^{\text{bulk}}, U^{\text{tet}} = 0.46 U^{\text{bulk}} \quad (\text{vi})$$

the reduction occurring because of the large change in co-ordination number. Both values used with equation (v) give  $D(M-\text{CO}) = 140\text{ kJ/mol}$ , and from equation (iii) we obtain  $b^{\text{oct}} = 136\text{ kJ/mol}$ , and  $b^{\text{tet}} = 173\text{ kJ/mol}$ , considerably more than the bond-energy in the bulk metal as one would expect in view of the large change in co-ordination number  $Z$  (7).

## General Conclusions

Physical measurements on transition metal cluster carbonyls suggest that there is a useful analogy to be made between these systems and chemisorbed carbon monoxide on the surface of the corresponding bulk metals. It is then natural to suppose that the transition metal d-electrons must play the dominant role in a theoretical description of the electronic structure of the cluster carbonyls, and in this review I have sketched the lines on which one can begin to build such a theory using recent developments in metal physics (7). It is to be expected that both chemical and physical properties of the platinum metal cluster carbonyls can be interpreted satisfactorily in this metal physics oriented framework.

## References

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