

Relativistic Phenomena in the Chemistry of the Platinum Group Metals

EFFECTS ON COORDINATION AND CHEMISORPTION IN HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

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It may at first sight seem strange that concepts developed by Albert Einstein in the first decade of the 20th century to explain the structure and dynamics of the cosmos should have any relevance to chemistry. However, it is now quite clear that the chemical behaviour of the heavier elements in particular is dominated by what are termed "relativistic effects". This article explores the implications of this for the coordination and chemisorption of carbon monoxide and unsaturated hydrocarbons, and their reactions in homogeneous and heterogeneous catalysis involving the platinum group metals.

A highly significant feature of the chemistry of the elements at the end of the three Transition Series of the Periodic Table is the close similarity that exists between the six elements with partially occupied $4d$ and $5d$ orbitals, that is, the group known as the "platinum metals", and the marked difference between them and the three elements which have only $3d$ electrons, that is, the base metals (iron, cobalt, nickel). This difference also extends into Group 11, where gold and silver are much "nobler" than copper. Part of the reason for this behaviour is that the size of the atoms increases on passing from the $3d$ to the $4d$ metals, but there is no further increase on going to the $5d$ metals, see Table I. This size difference is seen right across the Transition Series, from Group 4 to

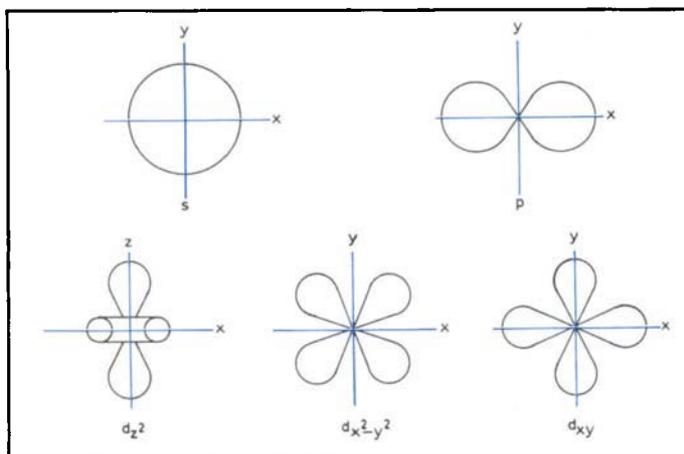
Group 10 and beyond, and it has traditionally been explained by electron occupation of the $4f$ orbitals to create the Rare Earth elements before the $5d$ orbitals start to be filled. This has been held to produce what is termed the "lanthanide contraction", caused by the inability of electrons in the $4f$ orbitals to shield effectively the s electrons from the increasing positive nuclear charge. The $6s$ orbital therefore contracts, and the expected increase in atomic size does not occur (1, 2).

Chemistry of the Heavier Elements

The heavier elements, that is, those having $5d$, $6s$ or $6p$ electrons, show a number of unusual physicochemical properties, many of which have been interpreted in terms of other measurable

Metal	Z	Electronic Structure	T_m , K	ΔH_{sub} , kJ mol ⁻¹	r, pm
Ru	44	(Kr) $4d^7 5s^1$	2655	648	132.5
Rh	45	(Kr) $4d^8 5s^1$	2239	556	134.5
Pd	46	(Kr) $4d^{10}$	1825	373	137.5
Os	76	(Xe) $5d^6 6s^2$	3318	784	133.7
Ir	77	(Xe) $5d^7 6s^2$	2713	663	135.7
Pt	78	(Xe) $5d^9 6s^1$	2042	469	138.5

Fig. 1 The forms of atomic orbitals:
 (i) *s* orbitals are spherically symmetrical
 (ii) *p* orbitals consist of three pairs of lobes, centred on each of the Cartesian axes (the p_x orbital is shown)
 (iii) *d* orbitals comprise the e_g family, that is the d_{z^2} and $d_{x^2-y^2}$ (shown), and the t_{2g} family, which contains three four-lobed orbitals centred on two of the Cartesian axes, each set being mutually at right angles (the d_{xy} set is shown)



parameters, such as ionisation potential, or by assigning a label, such as “the 6*s* inert pair effect”, which provides a comforting sense of understanding. However the underlying causes have remained uncertain, and there has been an increasing suspicion, especially in the last 20 years, that the lanthanide contraction is not a full, perfect and sufficient explanation for all that is observed. Among the anomalies are the greater stability of the Pt^{IV} oxidation state compared to Pd^{IV}, the stability of the Au^{III} state, the varied colours of the Group 11 metals, the low melting temperature of mercury and the existence of the Hg₂²⁺ ion.

Numerous other unexplained aspects of the chemistry of the heavier elements have been noted (1, 2). The quite startling properties of gold have recently been reviewed in depth (3): it has high electronegativity and can form the auride ion, Au⁻. It owes its nobility to the instability of its compounds with other electronegative elements, such as oxygen and sulfur.

The Relativistic Analogue of the Schrödinger Equation

The Schrödinger wave equation, describing subatomic particle motion, which we were taught to believe contained in principle the understanding of all chemistry, has in fact one major defect: it does not treat space and time as equivalent, as required by Einstein’s Theory of Special Relativity. P. A. M. Dirac and, independently, the Dutch physicist, H. A. Kramers, therefore devised a rela-

tivistic analogue of the Schrödinger equation, which incidentally predicted the existence of the positive electron (positron), and accounted for the occurrence of electrons having opposite “spins”. The difference which the relativistic correction made to the energetic description of the hydrogen atom was however very small, and it was therefore concluded that the chemical consequences were insignificant; but what was overlooked was the fact that, as the positive charge on the nucleus increases, the orbiting electrons must move faster in order to overcome the greater electrostatic attraction and hence to maintain their position. When the nuclear charge is about 50 (at the element tin), electrons in the 1*s* orbital are moving at about 60 per cent of the speed of light, and their mass is increased according to the equation:

$$m = m_0 (1 - v^2/c^2)^{-1/2}$$

where mass *m* moves with speed *v*, *c* is the speed of light and *m*₀ is the mass of the particle at rest. The 1*s* orbital therefore *contracts*, and the outer *s* orbitals have to contract in sympathy, but *p* orbitals are less affected, and *d* orbitals hardly at all: their shape determines that their electrons spend little time close to the nucleus, see Figure 1.

Relativistic Effects on the Properties of the Heavier Elements

The net effect of all this can be illustrated by the results of recent calculations for the metals molybdenum, tungsten and seaborgium, (4), see

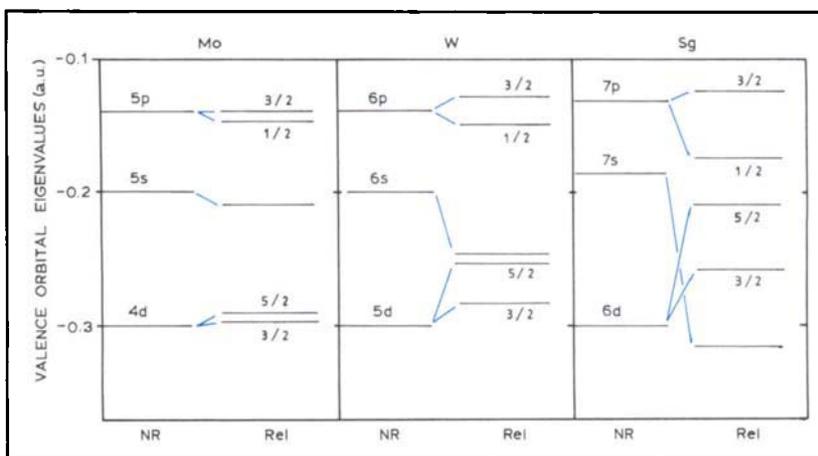


Fig. 2 This shows the calculated outermost atomic energy levels for molybdenum, tungsten and seaborgium (4), (assumed to be analogous to palladium, platinum and eka-platinum). The left-hand part for each element shows the non-relativistic values (NR) and the right-hand part the values having the relativistic correction (Rel)

Figure 2. We may provisionally assume this also applies to palladium, platinum and eka-platinum (element 110), respectively. The $6s$ orbital, having contracted, is thus lowered in energy, while the $5d$ levels are raised in energy because the orbitals have expanded. The spin-orbital splitting of the p and d orbitals is a particular feature of the relativistic treatment (5–7).

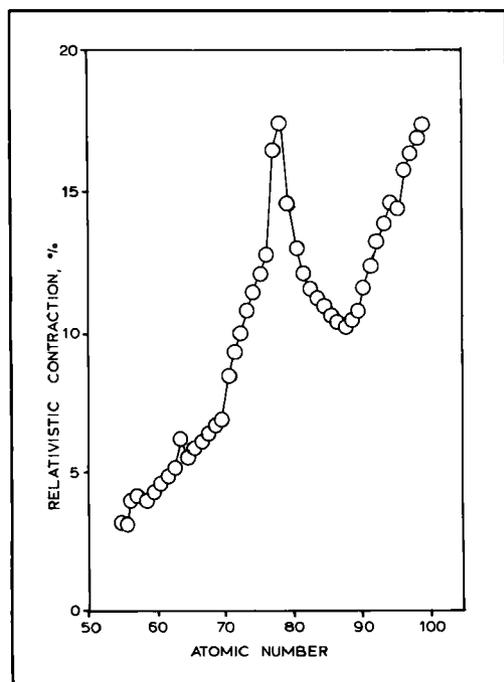


Fig. 3 Relativistic contraction of the $6s$ electron level as a function of nuclear charge (redrawn from (4))

The extent of the relativistic correction to the size of the s orbitals (and its smaller effect on p orbitals) increases approximately as the square of the nuclear charge, and the total effect on the atomic size is expressed as a “relativistic contraction”, that is, the fractional decrease in the actual metallic radius compared to the calculated non-relativistic value, see Figure 3. This relativistic contraction is greatest for platinum and gold, but it subsequently decreases with increase in nuclear charge as the space occupied by the $6s$ orbital has a diminishing effect on atomic size.

It is now generally thought that the relativistic contraction is at least as significant, if not more so, than the lanthanide contraction for the $5d$ metals, and that it is a dominant factor in the chemistry of elements having nuclear charge greater than 80 (mercury). From the energy level diagram of Figure 2 we can understand why the electron configuration of palladium is $4d^{10}$ while that of platinum is $5d^9 6s^1$, and why osmium and iridium have the $6s^2$ configuration while ruthenium and rhodium are $5s^1$ (because the lower energy levels are filled up first). It also follows that the $5d$ metals have *higher* ionisation potentials than the $4d$ (because the $6s$ level is of lower energy) and that they should have the greater bond strengths, with atoms both of different type and of the same type, as shown by the sublimation enthalpies and melting temperatures in Table I.

This also explains why the (100) and (110) surfaces of only the $5d$ metals undergo reconstruction

in the absence of chemisorbed atoms. The small difference in the energies of the $6s$ and $5d$ levels, Figure 2, means that d -electrons can be more easily removed or mobilised for bonding purposes, thus accounting for the stabilities of the Pt^{IV} and Au^{III} oxidation states. Indeed, it would be an interesting exercise to try to predict the properties of eka-platinum on the basis of calculated energy levels of the type shown in Figure 2.

The above observations and their interpretation have been well described (3, 5–7), so it is of more interest to explore less well documented areas. Inorganic textbooks (1, 2) pay due regard to the phenomenon of coordination of ligands to metal atoms and ions, and to the related reactions that occur in homogeneous catalysis, but little attention is paid to the parallel phenomenon of chemisorption or to the resultant reactions of heterogeneous catalysis. These are no less interesting, and in practical terms more useful, aspects of the inorganic/organometallic chemistry of the elements. We ought therefore to look for evidence of the operation of relativistic effects in these areas, to see whether they assist in understanding and in rationalising what is seen. This will be done by considering:

- carbonyl complexes, chemisorption of carbon monoxide and relevant reactions, and
- complexes and chemisorption of unsaturated hydrocarbons, and their reactions. In doing so it will be necessary to engage in some rather broad generalisations.

Coordination and Chemisorption of Carbon Monoxide

A very great deal of research has been performed on the carbonyls formed by coordination of carbon monoxide to metal atoms (1, 2). Stable neutral complexes containing one or more metal atoms exist for all the metals of Groups 8 to 10 *except* palladium and platinum, where the presence of either negative charge or of other ligands, such as halide ion, is required for stability. The same is true for the metals of Groups 11 and 12. Palladium is different from platinum, however, in that it cannot form polynuclear ionic complexes of the Chini type (8), but neutral monatomic complexes,

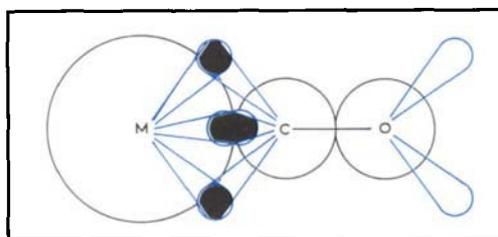


Fig. 4 Molecular orbital diagram for the linear bonding of carbon monoxide to a metal atom (14)

$M(CO)$, of both metals can be made at very low temperature using the matrix-isolation technique (9). The carbon monoxide can bond to one, two or three metal atoms, and the nature of the bonding is well understood (1, 2). In the linear form of coordinated carbon monoxide, the $5p$ molecular orbital donates charge to a vacant d orbital on the metal atom, and accepts charge from a filled atomic orbital into the 2π molecular orbital, Figure 4, but since both are antibonding the first strengthens the C-O bond and the second weakens it. The two effects therefore tend to cancel out, but the strength of the C-M bond depends on the extents of the two transfers of charge.

The role of the relativistic effect is shown by recent density functional theory (DFT) calculations on the first bond dissociation energy of carbonyl complexes of the type $M(CO)_5$ and $M(CO)_4$ (10), see Table II. The agreement between theory and experiment, where possible, is satisfactory. It is one of the triumphs of modern computational chemistry that results can be

Carbonyl	D , kJ mol^{-1}	
	Experimental	Calculated
$Fe(CO)_5$	176	192
$Ru(CO)_5$	118	138
$Os(CO)_5$	130	145
$Ni(CO)_4$	105	124
$Pd(CO)_4$	–	50.5
$Pt(CO)_4$	–	65.6

obtained on molecules such as $\text{Pd}(\text{CO})_4$ and $\text{Pt}(\text{CO})_4$ which do not exist as stable entities, although the calculation correctly predicts very low M-CO dissociation energies for them. Estimates of force constants for the Group 10 molecules $\text{M}(\text{CO})$ in matrix isolation provide confirmation that nickel is a much better σ -donor and π -acceptor than either palladium or platinum, although the latter is the second best because the destabilised $5d$ levels, see Figure 2, allow more metal-to-ligand back donation (9). In Group 8, both theory and experiment show that the sequence of M-CO bond energies is $\text{Fe} > \text{Os} > \text{Ru}$, for the same reason (10).

Much is also known about the chemisorption of carbon monoxide on metal surfaces and particles: the nature of the bonding is very similar to that in carbonyl complexes, and the fact that a surface metal atom is linked to a number of others seems to have little effect. The significant difference is however that the M-CO bond is stronger at surfaces than in complexes, so that strong chemisorption is observed with palladium and platinum, and the adsorbed state can even be studied on the Group 11 metals.

In fact, it is in Group 11 that the relativistic effect is more clearly seen (11–13), but results from a recent important paper which analyses the situation with the Group 10 metals in great depth must be examined (14). In summary it concludes that the chemisorption of a carbon monoxide molecule on platinum differs from that on nickel and palladium because there is:

- a larger differential shift in C-O vibration frequency between the atop and bridge sites, and
- a smaller change in the work function of the metal. These observations can only be explained theoretically on the basis of DFT calculations which incorporate the relativistic correction. This is however of much less importance in the case of palladium, see Figure 2.

Coordination of Hydrogen Atoms and Molecules

In homogeneously-catalysed reactions in which hydrogen is a reactant, it must first be coordinated to the metal centre: this usually occurs by dissociation and oxidative addition. The metals of Group

8 form complexes of the type $\text{M}(\text{PR}_3)_3\text{H}_4$ (15). When M is osmium there are four hydride ligands, but if M is iron or ruthenium there are two hydrides and one hydrogen molecule, the latter acting as a σ^* acceptor via its vacant antibonding σ^* orbital. DFT calculations show that this changeover is due to the destabilisation of the osmium $5d$ orbitals, making osmium a stronger donor. It is not yet known whether there are parallel differences in hydrogen chemisorption.

Homogeneous and Heterogeneous Catalytic Reactions of Carbon Monoxide

The industrially and environmentally important catalysed reactions of carbon monoxide are:

- (i) its reaction with hydrogen
- (ii) its reaction with hydrogen and an alkene, that is, hydroformylation
- (iii) its reaction with methanol, and
- (iv) its oxidation to carbon monoxide.

The reaction with hydrogen can lead to many different products, including methane, methanol and, by the Fischer-Tropsch synthesis, higher alkenes, alkanes and oxygenated products, depending on the catalyst used, and on the temperature and the pressure at which the reaction is conducted.

There are no significant applications of homogeneously catalysed reactions of carbon monoxide with hydrogen alone. Laboratory studies have shown that $\text{HCo}(\text{CO})_4$ can catalyse the formation of methanol, and rhodium cluster complexes can give 1,2-dihydroxyethane (ethylene glycol), but vigorous conditions are needed, and they are not commercially attractive (1).

All the many important reactions of carbon monoxide and hydrogen require heterogeneous catalysts. The metals which feature in Fischer-Tropsch synthesis are the three base metals of Groups 8 to 10, and ruthenium and osmium. Ruthenium is able to give very high molecular weight hydrocarbons at high pressure. Palladium can catalyse the formation of methane, and rhodium can make C_2 oxygenated products; the distinction here between these two metals and the others of Groups 8 to 10 is a clear reflection of the weaker bonding of carbon monoxide to their surfaces. In the same way, copper is the metal of choice for the industrial

synthesis of methanol, although gold also works, but much less effectively (3).

The carbonylation of methanol to acetic acid was for many years operated with a homogeneous rhodium catalyst, although an iridium compound is now also used (the *Cativa* process) (16). This is one of the very few examples of the use of iridium in industrial homogeneous catalysis.

Coordination and Chemisorption of Unsaturated Hydrocarbons

Much work has been performed on these subjects (1, 2, 17–19), so it is necessary to draw some broad generalisations and to select just a few examples for closer attention. Many metal atoms and ions coordinate alkenes, alkynes and alkadienes, and these molecules are also strongly chemisorbed by the metals of Groups 8 to 10.

Ethene

Most work has been done on ethene, so it will be discussed first. The archetypal complex is Zeise's salt, $K[PtCl_3(C_2H_4)] \cdot H_2O$, in which the ethene molecule coordinates sideways on to the Pt^{II} ion. The C-C bond is stretched and the hydrogen atoms move backwards, see Figure 5. The bond is very similar to that described above for carbon monoxide: electrons pass from a filled π orbital into a vacant d orbital on the metal (giving the σ component) and there is a reciprocal transfer back of electrons from a filled orbital into a vacant antibonding π^* orbital of the ethene (the π component). Similar coordination occurs with other metal atoms and ions of Groups 8 to 10, and with the univalent cations of Group 11, although here the bonding is weaker because there are no vacant d orbitals on the metal. There are also complexes of the type $M^0(PR_3)_2(C_2H_4)$ in which the geometry is distorted tetrahedral, see Figure 6. The bonding has predominantly π character, again because of the absence (in the case of palladium) or lesser availability (in the case of platinum) of d -orbital vacancies. The coordinated ethene molecule may therefore be considered to have a metallacyclopropane structure. The variable extents of the two types of orbital overlap, depending upon the electronic structure of the

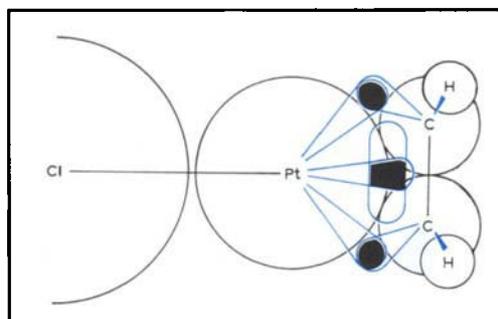


Fig. 5 Molecular orbital diagram for the bonding of ethene to Pt^{II} in $[PtCl_3(C_2H_4)]^-$ (the anion of Zeise's salt). Note that there are other Cl^- ions in front of and behind the platinum atom

metal species, the nature of the other ligands and the substituents on the alkene, mean that there is a continuous range of structures, from an almost unaltered ethene molecule through the $\sigma\pi$ complexed Zeise's salt structure to the ethane-like metallacyclopropane mode, rather than there being clearly divided classes.

It is difficult to find quantitative information on the strengths of the coordinate bond between ethene and metal atoms or ions. There is however a general impression that platinum complexes are more strongly bonded than palladium, due to the greater spatial extension of the platinum's $5d$ orbitals, and the larger orbital overlap which is therefore possible. This impression is confirmed

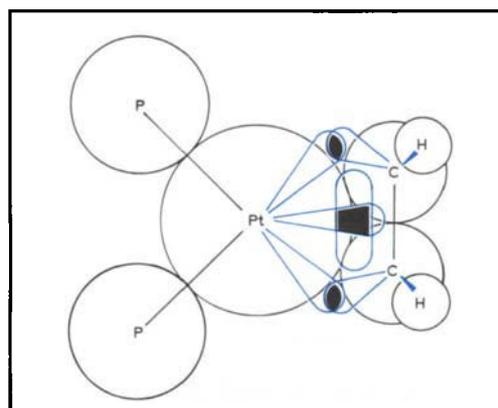


Fig. 6 Molecular orbital diagram for the bonding of ethene to Pt^0 in $Pt^0(PPh_3)_2(C_2H_4)$: electron donation from ethene is supposed to be to a partly-filled dp^2 hybrid orbital on the metal. This complex is almost planar; the phenyl groups are not shown

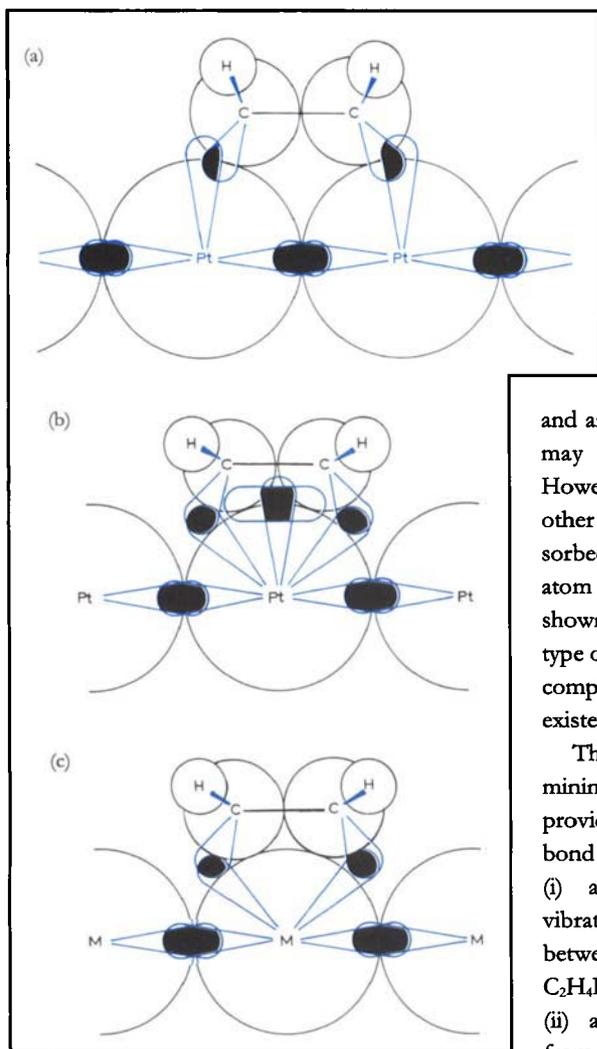
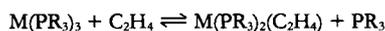


Fig. 7 Molecular orbital diagrams for ethene chemisorbed on metal surfaces: (a) the σ -diadsorbed form on platinum, (b) the $\pi\sigma$ form on a platinum atom (the analogue of the structure shown in Fig. 6) and (c) on atoms of Group 11, where back-bonding from ethene to metal cannot occur because of the lack of a suitable vacant orbital

by measurements of the equilibrium constant for the formation of $M(PR_3)_2(C_2H_4)$ complexes in benzene solution at 298 K:



the values of which are ~ 300 for nickel, 0.013 for palladium and 0.122 for platinum (20). Bond energies for these complexes and for those of the type $M(CO)_4(C_2H_4)$ have been calculated by relativistic

DFT, and are, in both cases, smallest for palladium, see Table III, (21).

Similar structures to those seen in coordination complexes have also been identified when ethene is chemisorbed by metal surfaces or particles (17–19). Indeed, a simple-minded theoretical basis for the correspondence was presented in the mid-1960s (22). In particular the $\pi\sigma$ form (as in Zeise's salt) is seen at low temperature or high surface coverage on a number of surfaces,

and an analogue of the metallacyclopropane form may also have been detected, see Figure 7. However, because multi-atom sites are available, other structures can arise, especially the σ -diadsorbed ethane-like structure where each carbon atom forms a σ -bond to two metal atoms, as shown in Figure 7, (23). The only analogy for this type of structure in organometallic chemistry is the complex $Os_2(CO)_8(C_2H_4)$, which may also owe its existence to the relativistic d orbital destabilisation.

The use of spectroscopic and structure-determining techniques such as FTIR and LEED have provided estimates of the stretching of the C-C bond following chemisorption, either by:

- (i) a " π,σ parameter" derived from the change in vibration frequency of the C-C bond, taking values between zero (for the free molecule) and unity (for $C_2H_4Br_2$) (24), or by
- (ii) a bond order between unity and two derived from the length of the C-C bond (19).

Some values of both parameters are given in Table IV, and show that the distortion due to stretching is slight for the Group 11 metals but large for iron, ruthenium, nickel and platinum surfaces.

From the very extensive literature, the following generalisations may be made:

- (i) The σ -diadsorbed form of ethene is commonly seen on platinum surfaces, but rarely on palladium, which usually shows the $\pi\sigma$ type of structure.
- (ii) The $\pi\sigma$ type occurs together with the σ -diadsorbed form on stepped platinum surfaces.
- (iii) Pre-adsorbed oxygen atoms favour the $\pi\sigma$ form, or structures which tend towards this form. The clear conclusion is that here is a marked

tendency for ethene to be more strongly chemisorbed (as the σ -diadsorbed form) on platinum than on palladium (where the $\pi\sigma$ form is favoured); the parallels with coordination chemistry are also very marked, and the explanations are the same.

Other Alkenes

Alkenes having a methylene group adjacent to the double bond may on coordination lose a hydrogen atom to form a π -allylic ligand (1, 2). This occurs with a number of metal atoms and ions, but more readily and extensively with nickel and palladium than with platinum. Here is another distinction that may have its origin in relativistic effects. Dienes coordinate strongly through both double bonds to many metal species, for instance, on palladium, 1,3-butadiene is chemisorbed by both double bonds in the $\pi\sigma$ mode, but on platinum, only through one double bond in the σ -diadsorbed form (18).

Homogeneous and Heterogeneous Catalysis of Reactions of Unsaturated Hydrocarbons

It would be possible to summarise the homogeneous catalysis of alkene reactions and of metal-mediated reactions of organic molecules in general by saying simply that (with the sole exception of hydrosilylation) *all require a metal compound or complex drawn from the elements in the first two rows of Groups 8 to 10*. This remarkably clear generalisation

Table III Ethene-Metal Bond Dissociation Energies Calculated by Relativistic Density Functional Theory (21)	
Complex	Bond dissociation energy, kJ mol ⁻¹
Ni(PH ₃) ₂ (C ₂ H ₄)	38.0
Pd(PH ₃) ₂ (C ₂ H ₄)	19.8
Pt(PH ₃) ₂ (C ₂ H ₄)	22.8
Ni(CO) ₄ (C ₂ H ₄)	38.9
Pd(CO) ₄ (C ₂ H ₄)	30.7
Pt(CO) ₄ (C ₂ H ₄)	39.3

Table IV

Values of the π,σ Parameter (24) and of the C-C Bond Order (19) for Ethene Chemisorbed on Various Metal Surfaces

Surface	π,σ Parameter	Bond order
Fe(110)	0.55	1.20
Ru(001)	0.85	1.35
Rh(111)	0.50	1.39
Ni(111)	0.80	1.33
Pd(111)	0.43	1.61
Pt(111)	0.92	1.13
Cu(100)	0.21	1.66
Ag film	-	1.88
Au foil	0.25	-

is however not often noted. The distinction between the second and third row metals is strikingly confirmed by inspecting, for example, Number 3 of this Journal for 1999, where in the reviews on pages 103 and 114, and in the Homogeneous Catalysis' Abstracts and New Patents sections, every reference concerns either ruthenium, rhodium or palladium. More generally, complexes of the three base metals: iron, cobalt and nickel, are also effective, while those of the 5d metals and compounds of the Group 11 metals are not. This illustrates the operation of a "Volcano Principle" in homogeneous catalysis: the 5d metals form complexes that are too strong, the Group 11 metal complexes are too weak, while those of the 3d and 4d metals fall in the acceptable range. Unfortunately there seems to be little *quantitative* information available (apart from that mentioned above) to underpin that statement.

It is only necessary to record briefly some of the observations which lead to this concept. Early work on homogeneous hydrogenation used compounds or complexes of iron, cobalt, ruthenium and rhodium (for example, Wilkinson's complex Rh(PPh₃)₃Cl); hydroformylation used initially cobalt, but this was later replaced by rhodium which gave greater selectivity to terminal aldehydes (2). Complexes of Ni^{II} and Rh^I catalyse the dimerisation of alkenes (2), and complexes of Fe^{II}, Ni^{II} and Pd^{II} with suitable nitrogen-containing ligands catalyse the polymerisation of ethene either

to α -alkenes or to high-density polyethylene, depending on the type of ligand (25). Ni^{II} complexes also polymerise ethyne to either benzene or cyclo-octatetraene.

In the case of hydrosilylation, the use of platinum is probably required in order that an alkene complex of sufficiently great stability can be formed in the presence of bulky $-\text{SiR}_3$ ligands.

Alkenes coordinated to nickel and palladium species are susceptible to nucleophilic attack, for example by OH^- ions. The best-known case of this is the oxidation of ethene by Pd^{II} to ethanal (acetaldehyde), or in the presence of ethanoic (acetic) acid to ethenyl ethanoate (vinyl acetate). Here the Pd^{II} is reduced to Pd^0 , and an oxygen-carrying Cu^{II} species is needed to complete the catalytic cycle (1, 2).

In heterogeneous catalysis, the clearest proof of the operation of a relativistic effect lies in the reactions of unsaturated hydrocarbons with hydrogen or deuterium. There is a very clear distinction between:

(A) nickel and palladium (and copper) on the one hand, and

(B) platinum (and iridium) on the other, in the following reactions (26):

(i) Reaction of ethene with deuterium, where the A Group metals allow a much greater return of deuterium-substituted alkenes to the gas phase.

(ii) Reactions of C_4 or higher alkenes where molecules altered by double-bond migration or *E/Z*-isomerisation appear in the gas phase to a much greater extent with the A Group than the B Group.

(iii) Hydrogenation of alkynes and alkadienes, for which the A Group metals are more active, and on which they afford the intermediate alkene with much higher selectivity, and preferential *Z*-addition of hydrogen; with 1,3-butadiene, for example, a high yield of 1-butene is obtained.

All of these observations are consistent with a weaker chemisorption of the alkene compared to that of the alkyne or alkadiene on the A Group metals, as indeed was suspected many years ago (26). These and other features of the reaction have been rationalised by proposing that $\pi\sigma$ or π -allylic intermediates occur with the A Group, but σ -

diadsorbed intermediates with the B Group. Once again there is a clear correspondence between the findings of organometallic chemistry and homogeneous catalysis and with those of heterogeneous catalysis.

The second point (ii) above also explains why fat-hardening is conducted with nickel (27) or palladium (28) catalysts, but not with platinum. Expressed briefly, a C_{18} chain containing three non-conjugated $\text{C}=\text{C}$ bonds has to be hydrogenated so that only one $\text{C}=\text{C}$ bond is left. This requires first an isomerisation to bring them into conjugation, and then a selective hydrogenation, for which nickel under hydrogen-diffusion-limited conditions is suitable. Palladium is also suitable.

We may also note that ethyne trimerises to benzene on palladium (best on the (111) surface), just as occurs with Ni^{II} complexes (29).

Finally we may ask why platinum was the metal of choice for petroleum reforming, since the opening step is dehydrogenation of an alkane, followed by desorption of an alkene and its migration to an acid site. In fact nickel was the metal first used, and recently palladium has found some use, so the answer probably lies in the fact that platinum, in conjunction with tin or rhenium, is much less susceptible to deactivation by carbon deposition than nickel or palladium would be.

Some Final Thoughts

This review has indicated that there are many respects in which the *5d* metals (Os, Ir, Pt, Au) differ from the *3d* base metals (Fe, Co, Ni, Cu) and the *4d* metals (Ru, Rh, Pd, Ag) (30). These differences can be explained in terms of the stabilisation of the *6s* level and the destabilisation of the *5d* level, compared to the situation in the earlier series, see Figure 2. The origin of this phenomenon is the operation of a relativistic effect on all the *s* orbitals. Metal catalysts for those reactions involving only σ -bonded alkyl radicals or multiple $\text{C}=\text{M}$ bonds (equilibration of alkanes with deuterium, alkane hydrogenolysis, etc.) do not show preferential activity related to this effect.

It may be wondered what other aspects of the chemistry of the elements may be traced to this cause. In the bioinorganic field, there is platinosis,

but not palladosis; there is the well-known toxicity of many of the heavy elements, but the beneficial use of platinum complexes in chemotherapy (7) (but not so much those of palladium or other metals) and of gold (but not silver) in treating arthritis. It would be surprising if there were not some underlying connection.

So next time you touch gold, or drive a car with a platinum catalyst beneath it, or take your temperature with a mercury-in-glass thermometer do remember: you are now directly in touch with some consequences of the principles that shape the Universe and are determining its evolution.

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Platinum Films in Gasochromic Switched 'Smart' Windows

The solar light and heat allowed into a building can be controlled by WO₃-film 'smart' windows. Optical modulation is used to 'switch' such films to control the frequencies transmitted. Switching can be done in different ways. WO₃ films prepared by sputtering have fast colouring/bleaching kinetics, but textured surfaces. Sol-gel-made films have higher visible transmittance in the bleached state and thicker films are easier to make.

Now work from the National Institute of Chemistry, Ljubljana, Slovenia, and the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany, combines sputtering and sol-gel meth-

ods: to make WO₃ film, with platinum catalyst sputtered on the surface and atomic hydrogen (gasochromism) to 'switch' them (U. Opara Krašovec, B. Orel, A. Georg and V. Wittwer, *Solar Energy*, 2000, 68, (6), 541–551).

Sol-gel WO₃ films were made by dip-coating. Adding an ormosil gave thicker, less brittle films of improved coloration. The sol-gel/Pt(sputtered)WO₃ films change colour as quickly as Pt/WO₃ sputtered films, and faster than WO₃ sol-gel films with Pd. In H₂/Ar gas mixtures the films colour in H₂ concentrations as low as 0.002 per cent. This may give simpler switchable 'smart' windows.