

Review

# Relativistic effects in coordination, chemisorption and catalysis

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## Abstract

Relativistic effects dominate the chemistry of elements of atomic number greater than about 50: *s* electron shells are contracted and lowered in energy, while *d* shells are destabilised; differences between the second and third row Transition Series elements are now only partly ascribable to the ‘lanthanide contraction’. Relativistic effects on the chemistry of gold, on the surface structures of metals and on the structure, stability and reactivity of carbonyl and hydrocarbon complexes are surveyed, and their consequences in homogeneous and heterogeneous catalysis, hitherto unrecognised, are explored. Reactivity of organometallic complexes is very largely confined to those containing a metal from Groups 8–10 of the first two Transition Series: complexes of Group 11 metals are too weak, and of the third Transition Series too strong, to be useful. In heterogeneous catalysis, methanol synthesis is observed with metals (Au, Cu, Pd, Pt) not forming stable carbonyls, the other metals of Groups 8–12 giving Fischer–Tropsch products with syngas. In reactions of unsaturated hydrocarbons, all palladium catalysts readily release intermediate alkene products to the fluid phase, but platinum catalysts do not. These and related differences are due to the weaker  $\pi$ -alkene and  $\pi$ -allylic intermediates, which form on palladium. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

### 1.1. An outline of the basic theory [1–11]

It is generally thought that the Schrödinger wave equation contains, at least potentially, the solution to all chemical problems. However, as P.A.M. Dirac noted in 1928 [1–3], it does not treat space and time in equivalent ways (i.e., it

is not Lorentz–Fitzgerald invariant), and it assumes by implication that light has an infinite velocity. He therefore devised a relativistic analogue of the Schrödinger equation for the H atom, which does not have these defects: its solution automatically predicts the existence of the positron, and accounts for the occurrence of opposing spins in electrons [7]. It also gives orbital forms that do not have nodes at the nucleus, so the taxing question of how different lobes communicate is avoided. It appears that the Dutch physicist H.A. Kramers also devel-

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oped an equivalent treatment at about the same time, although his work is less well known [12].

Dirac did not feel that changing to a relativistic wave equation would have any important consequences for chemistry, since the effect for the H atom is very small. However, in the case of the heavier elements the inner electrons feel a large nuclear charge, and in order to maintain balance with the strong electrostatic field they must acquire speeds that are comparable with that of light [6]. If their speed is  $v$  and that of light is  $c$ , their mass  $m$  is increased relative to their rest mass  $m_0$  as determined by the equation

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

which follows from Einstein's Theory of Special Relativity. The effect, which in principle exists in all atoms [6,7], increases roughly as the square of the atomic number  $Z$  and begins to be important when  $Z$  exceeds about 50 (Sn): thus, for Au ( $Z = 79$ ) and Hg ( $Z = 80$ ) the  $1s$  electrons have speeds which are about 58% that of light, and their mass is therefore some 20% greater than their non-relativistic mass. The  $1s$  orbital is therefore shrunk, and the  $s$  orbitals of higher quantum number contract in sympathy, in order to maintain orthogonality: the fractional contraction of the  $6s$  shell is in fact greater than that of the  $1s$ . The same occurs to  $p$  electrons, but to a lesser extent;  $d$ - and  $f$ -orbitals are, however, scarcely affected, because their electrons never come close to the nucleus due to the centrifugal potential  $l(l+1)/r^2$ . Furthermore, their effective potential is more efficiently screened because of the relative contractions of the  $s$  and  $p$  shells; they, therefore, increase in energy and move outwards radially. This is the *indirect relativistic orbital expansion*.

This contraction of radius and energetic stabilisation experienced by  $s$  and  $p$  electrons, and the expansion of radius and energetic destabilisation of  $d$  and  $f$  electrons, is accompanied by orbital splitting of the orbitals for which  $l$  is greater than zero, and this effect increases

markedly with atomic number. Approximate relativistic energy levels for the outer electrons of the elements of Group 6 (Mo, W and Sg (seaborgium)) are compared with non-relativistic values in Fig. 1 [13].

It is an undeniable fact that there is a much greater similarity between the physics and chemistry of the second and third Transition Series elements than between those of the first and second (Table 1). In the past, this has been attributed to the 'lanthanide (or lanthanoid) contraction', that is, the failure of the  $5d$  and  $6s$  electron shells to occupy the expected space because the  $5f$  electrons do not adequately shield them from the increasing nuclear charge, by reason of the shape of their orbitals:  $5d$  and  $6s$  electrons are, therefore, drawn towards the nucleus. A similar but much weaker effect has been proposed for the effect of  $d$ -electrons on  $s$ -electron shells in the earlier Transition Series [6]. It is, however, now an open question as to how much of the observed effect is due to this 'lanthanide contraction', and how much to the relativistic effect outlined in the last paragraph. It appears that the two are now regarded as being of comparable importance, at least in determining the sizes of atoms and ions in the third Transition Series. The relativistic phenomena do, however, lead to *selective* effects on the sizes and energies of the various electron shells, and as we shall see account for chemical behaviour that is not otherwise explicable.

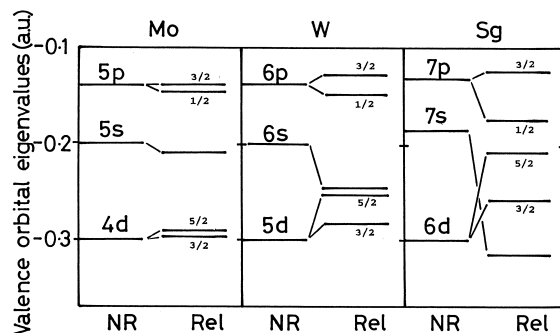


Fig. 1. Calculated outermost atomic energy levels for molybdenum, tungsten and seaborgium (redrawn from Ref. [13]).

Table 1  
Some physical properties of the elements of Groups 8 to 12

Property	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt	Cu	Ag	Au	Zn	Cd	Hg
Metallic radius (pm)	124.1	132.5	133.7	125.3	134.5	135.7	124.6	137.5	138.5	127.8	144.47	144.20	133	148	150
$T_m$ (K) <sup>a</sup>	1808	2655	3318	1768	2239	2713	1726	1825	2042	1356	1234	1337	692	594	234
$T_b$ (K) <sup>b</sup>	3020	4320	5300	3370	4033	4820	3190	3210	4443	2843	2428	3081	1180	1038	630
$\Delta H_{\text{sub}}$ (kJ mol <sup>-1</sup> ) <sup>c</sup>	416	648	784	425	556	663	430	373	469	337	285	379	131	112	61
First IP (kJ mol <sup>-1</sup> ) <sup>d</sup>	759	710	820	758	720	868	560	804	866	745	731	890	906	876	1006

<sup>a</sup>Melting temperature.

<sup>b</sup>Boiling temperature.

<sup>c</sup>Enthalpy of sublimation.

<sup>d</sup>First ionisation potential.

It is possible to calculate the size of the relativistic effect and its variation with nuclear charge [5,6]. The ‘relativistic contraction’, that is, the fractional decrease in the size of the  $s$  orbital compared to its calculated non-relativistic value, has been given for the  $6s$  shell in the third long period and beyond [6,7]. It increases slowly from  $Z = 55$  to  $Z = 70$ , then more rapidly to  $Z = 78$ : there is a sharp maximum at platinum (78) and gold (79), where the contraction is about 17%, before it falls again to  $Z = 90$ , whereafter it again rises. A very noticeable consequence of this maximum is that the fractional change in metallic radius between the second and third row metals is about +0.9% in Groups 8 and 9, +0.7% in Groups 10 and 12, but –0.2% in Group 11 (see Table 1). There is now no doubt that gold atoms and ions are *smaller* than those of silver [9,14,15]. The greater rate of increase in the contraction after  $Z = 70$  arises from the relativistically-enhanced loss in nuclear screening ability of both the  $5d$  and  $4f$  electrons [9].

### 1.2. Consequences for inorganic chemistry

The effects described above have important consequences for the inorganic chemistry of the heavier elements, and they completely dominate the character of elements beyond bismuth [13]. Growing awareness of this is signalled by a rapidly increasing literature, and the holding of a European Research Conference on ‘Relativistic Quantum Chemistry’ in April 1999. The relevance of the large spin-orbit coupling to the interpretation of magnetic [4–6] and spectroscopic [7] properties of their clusters and compounds is profound, but will not be developed here, as it has no close connection with the matter in hand. The most dramatic effects are on the properties and compounds of gold: these will be dealt with in Section 2.1. The stability of the  $6s^2$  configuration is well known; it is a direct consequence of the relativistic phenomenon [6,13], and accounts for the stability of lower oxidation states such as  $Tl^I$  and  $Pb^{II}$ .

Other observations only explained within this framework include the dimeric form of the mercurous ion  $Hg_2^{2+}$ , which contrasts with the monomeric forms shown by  $Cu^I$ ,  $Ag^I$  and  $Au^I$ , and the unusual structure shown by mercury in the solid state: it is of course the only metal that is liquid at 298 K

It is not the purpose of this review to provide detailed explanations for these observations, because these are fully revealed in the cited references [4–9,13], together with many more examples of the importance of relativistic effects in chemistry. The few quoted cases are intended to show to those who have not yet met the consequences of relativity that it does indeed offer a rational basis for understanding major features of the chemistry of the heavier elements [13,16,17], some of which (e.g., Ir, Pt, Au, Sn, Bi) have useful properties in both homogeneous and heterogeneous catalysis. Some further attention will therefore be given in Section 2 to the properties of the metals in Groups 10–12. It will be interesting to see how far relativistic effects may be responsible for the ways in which the catalytic properties of the heavier metals differ from those of their lighter predecessors.

## 2. Relativistic effects on the physicochemical properties of metals

### 2.1. Group 11

Gold is unique in its physicochemical properties, which are unpredictable by extrapolation from those of its neighbours (Tables 1 and 2) [16–20]. It is the most electronegative metal, comparable to selenium, and only slightly more electropositive than sulfur and iodine: its electron affinity is actually greater than that of oxygen, and the  $E^\circ$  value for the  $Au^+/Au^0$  couple has the very high value of +1.691 V. These properties explain the instability of its compounds with other electronegative elements such as sulfur and oxygen, and hence, account

Table 2  
Some properties of the metals of Group 11 [21,22]

Property	Copper	Silver	Gold
M <sub>2</sub> dissociation energy (kJ mol <sup>-1</sup> )	196	160	223
M <sub>2</sub> equilibrium bond length (nm)	0.222	0.253	0.247
M <sub>3</sub> dissociation energy (kJ mol <sup>-1</sup> )	294	253	367
MH dissociation energy (kJ mol <sup>-1</sup> )	266	220	311
<sup>2</sup> S → <sup>2</sup> d excitation energy (kJ mol <sup>-1</sup> )	133	361	109
Electronic specific heat <sup>a</sup>	6.926	6.411	6.918
Thermal conductivity <sup>b</sup>	3.85	4.18	3.1
Specific resistivity <sup>c</sup>	1.72	1.62	2.4

<sup>a</sup>10<sup>-4</sup> J mol<sup>-1</sup> K<sup>-1</sup> below 4 K.

<sup>b</sup>J K<sup>-1</sup> cm<sup>-1</sup> s<sup>-1</sup> at 273 K.

<sup>c</sup>10<sup>-8</sup> Ω m at 293 K.

for its reputation of ‘nobility’: the contrast with silver could not be more marked. Its electronegativity is also shown by the stability of the auride ion Au<sup>-</sup>, which exists in liquid ammonia and in salt-like compounds such as Cs<sup>+</sup>Au<sup>-</sup> [5–9]. The behaviour of gold is, therefore, somewhat reminiscent of that of a halogen. These aspects of its chemistry are a consequence of the stability of the 6s<sup>2</sup> configuration (‘inert pair effect’), which is explained by the relativistic contraction of this electron shell [5,6,9,20,21]. The resulting high value of the first ionisation potential (Table 1) dictates that the chemistry of the Au<sup>I</sup> state is much more limited than those of Cu<sup>I</sup> and Ag<sup>I</sup>; the Au<sup>+</sup> ion is unstable in solution, disproportionating into Au<sup>0</sup> and Au<sup>3+</sup>.

The Au–Au bond as shown by the enthalpy of sublimation, and by the melting and boiling points of the element (Table 1), is stronger than the Ag–Ag bond but similar to the Cu–Cu bond. This trend is also demonstrated by the dimers and trimers [22] (Table 2). In addition to accounting for interatomic distance and density,

relativistic effects also explain gold’s relatively high specific resistivity, the correspondingly low thermal conductivity (the two being related by Wiedemann–Franz Law) and its electronic specific heat (higher than for silver) (Table 2) [21]. The yellow colour of gold, similar to that of copper but different from that of silver, caused by optical absorption in the visible region, is due in turn to the relativistic lowering of the gap between the 5d band and the Fermi level [18]. In the absence of this effect, gold would be white like silver, and have the same propensity to tarnish and corrode.

A further striking characteristic that distinguishes gold from the other Group 11 elements is the ease with which it forms Au–Au bonds in organometallic clusters [16,23]: multinuclear clusters are few for copper and are very rare with silver.

A further consequence of the 6s orbital contraction and the associated 5d orbital expansion is that the difference between the energies of these levels is lowered (Fig. 1); the 5d electrons are, therefore, more easily mobilised for bonding purposes. This explains the more frequent occurrence of the Au<sup>III</sup> state compared to Cu<sup>III</sup> and Ag<sup>III</sup>, and the existence of the Au<sup>IV</sup> and Au<sup>V</sup> states in complexes with the very electronegative F<sup>-</sup> ion [20,21]. For more detailed and profound interpretations of what is observed, the cited references [5–9,13,21] should be consulted.

## 2.2. Group 12

Many of the same trends as shown in Group 11 are found here as well. The Hg–Hg bond is, however, very weak compared to the bonds in zinc and cadmium; this is also a result of the stabilisation of the 6s<sup>2</sup> ‘lone pair’, as are its resistance to corrosion, the instability of the oxide and its positive electrode potential derived from the s shell contraction, as with gold. The closely similar metallic radii of cadmium and mercury, and the stability of the dimeric mercurous ion Hg<sub>2</sub><sup>2+</sup> (isoelectronic with Au<sub>2</sub>), find

their explanation in the same effect. The existence of the  $\text{Hg}^{\text{I}}$  state in  $\text{Hg}_2^{2+}$  stands in contrast to the very limited occurrence of the  $\text{Zn}^{\text{I}}$  and  $\text{Cd}^{\text{I}}$  states.

### 2.3. Group 10

Certain of the trends shown here resemble those in Group 11. The Pt–Pt bond is stronger than the Ni–Ni and Pd–Pd bonds, the weakness of the latter corresponding to that in silver (Table 1). While platinum exhibits both the  $\text{Pt}^{\text{II}}$  and  $\text{Pt}^{\text{IV}}$  states, the higher oxidation state in palladium is less stable than in platinum, and the great majority of palladium complexes and compounds involve either  $\text{Pd}^0$  or  $\text{Pd}^{\text{II}}$ .

Apart from its contribution to the restricted increase in size on going from the second to the third Transition Series (Table 1), the relativistic contraction has less obvious effects in the earlier Groups 8 and 9.

### 2.4. Metal–metal bonding and the surface structures of metals

There are a number of indications of the intrusion of relativistic effects in the results of structural studies on single crystals of metals. It is well-known that adsorbate-induced reconstructions occur with many surfaces, leading to structures which minimise surface energy [24–26], but reconstruction of the (100) surface of face-centred cubic metals to give an hexagonal overlayer having the trigonal symmetry of the (111) plane is apparently limited to iridium, platinum and gold. Vicinal structures on the Au(100) surface have been studied by STM [27]. A similar transformation of the (110) surfaces of the third row fcc metals to a more corrugated surface exposing larger (111) facets is also motivated by considerations of minimum surface energy [24]. The striking fact that these changes are not found with rhodium, palladium or silver is probably due to their having lower enthalpies of sublimation and, therefore, lower surface energies. With the *5d* metals, having

higher surface energies, there is a greater driving force to minimisation by reconstruction: this can, therefore, be directly linked to the relativistic influence on the outer electron shells.

A further example of the importance of relativistic effects is provided by density-functional calculations on cluster models of atoms of Groups 10 and 11 on the (100) surface of aluminium [28]. The bonds are found to be largely covalent, with small charge displacements and, therefore, small dipole moments, the sign of which is, however, in the opposite sense for platinum and gold to that of the others. This was attributed to ‘intra-atomic relativistic effects’.

A five-layer slab calculation of the Knight shift for platinum requires relativistic corrections to obtain agreement with experiment [29,30].

## 3. Coordination and chemisorption of carbon monoxide

### 3.1. General survey

Carbonyl complexes formed by metal atoms, metal ions and clusters have been comprehensively studied, and the chemisorption of carbon monoxide on metal surfaces has proved a rewarding field of study: the vibration frequency of the C–O bond responds sensitively to the nature of the atom(s) to which the molecule is bound and to the presence of other adsorbed species. Stable neutral carbonyl complexes are formed by the metals of Groups 8 and 9, and by nickel, but not by palladium, platinum, or the metals of Groups 11 and 12. For these last metals the presence of either negative charge (as in the polynuclear ‘Chini’ complexes of platinum [23]) or of other ligands such as halide ion are required for stability [16]. Neutral carbonyl complexes of copper, silver, palladium and platinum have, however, been prepared and studied at very low temperatures by the matrix-isolation technique [31–33]. These limitations do not pre-

vent the strong chemisorption of the molecule on the surfaces of palladium and of platinum, and its adsorption on copper, silver and gold, although weaker, is strong enough to allow experimental study. Polynuclear carbonyl clusters are formed by all the metals of Groups 8–10, including platinum, and especially by rhodium and osmium, but not palladium [34].

The usefulness of carbon monoxide as a probe for surface structure and reactivity has been greatly enhanced by the close analogies that exist between chemisorption and coordination. In both situations the molecule can react either linearly with a single metal atom, or in a bridge form with a pair of atoms, or it may occupy a three- or a four-fold site: only the last has no analogy in complex chemistry. Electrons flow from the  $5\sigma$  anti-bonding orbital of the molecule to a vacant orbital on the metal atom, and a reverse flow occurs from the metal into the  $2\pi$  antibonding molecular orbital: neither the  $4\sigma$  nor the  $1\pi$  orbital appears to be involved [35]. The first movement, therefore, strengthens the C–O bond and the second weakens it: which dominates therefore depends on the nature of the metal and its coordination number. Nickel is much better both as a  $\sigma$ -donor and a  $\pi$ -acceptor than either palladium or platinum (it has the lowest first ionisation potential in Group 10 (Table 1) and also the smallest energy requirement for  $d^{10}$  to  $d^9p^1$  promotion), this accounting for the stability of  $\text{Ni}(\text{CO})_4$  and the instability the carbonyls of the other metals [16]. The weaker bonds formed by the metals of Group 11 result from the absence of vacant metal orbitals, the  $(n-1)d$  orbital lying well below the  $ns$  level, so that the bond has mainly  $\pi$ -character.

The carbon monoxide molecule can dissociate entirely on the surface of a number of metals, but this does not occur to any extent with the metals of Groups 9–11.

### 3.2. Relativistic effects in the coordination of carbon monoxide

We may now search for quantitative evidence of relativistic factors being at work in carbonyl complexes: a particular symptom will be the absence of monotonic changes in thermochemical or structural parameters on passing down a particular Group of the Periodic Classification. First-bond dissociation energies have been calculated [36] using a non-local quasi-relativistic density-functional method for complexes of the formulae  $\text{M}(\text{CO})_6$ ,  $\text{M}(\text{CO})_5$  and  $\text{M}(\text{CO})_4$  for the three Transition Series, and the results compared with experimental values (Table 3): agreement is satisfactory in most cases. In Groups 6 and 8, both theory and experiment show an increase in stability from the second to the third Series, caused by an increase in metal-ligand back donation raising the energy of the  $d$ -levels. In Group 10, theory reproduces well the low stability of the carbonyls of palladium and platinum, the former being the less stable. A ‘scalar relativistic version of the linear combination of Gaussian-type orbitals with the density-functional method’ has been applied [37] to the monocarbonyls  $\text{M}(\text{CO})$  of Group 10 (Table 4): for these complexes, formed at low temperature by the matrix isolation technique [32,33], the same trend holds, namely, the  $\text{Pd}(\text{CO})$  molecule has a much weaker M–C bond than the others.

Table 3

Calculated and experimental first bond dissociation energies of mononuclear carbonyl complexes ( $\text{kJ mol}^{-1}$ ) [36]

Electron shell	$\text{M}(\text{CO})_6$		$\text{M}(\text{CO})_5$		$\text{M}(\text{CO})_4$	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
3d	194	154	192	176	125	105
4d	166	170	138	118	50.5	–
5d	183	193	145	130	65.6	–

Table 4  
Calculated properties of the monocarbonyl compounds M–CO of the Group 10 metals [37]

Metal	M–C length (nm)	$\omega_0(\text{M–C})$ ( $\text{cm}^{-1}$ )	$D_c^a$ ( $\text{kJ mol}^{-1}$ )
Ni	0.168	612	249
Pd	0.186	462	203
Pt	0.178	627	338

<sup>a</sup>Dissociation energy.

Carbon monoxide reacts with neutral diatomic clusters of copper and gold formed in the gas phase, but not with  $\text{Ag}_2$  [22]: reaction of  $\text{Au}_2$  is much faster than with  $\text{Cu}_2$  and the resulting complex is stabler. Anionic clusters have been formed in a ‘flowing afterglow ion source with a cold cathode dc discharge’ [38]; reaction with carbon monoxide occurs with copper and gold, but not with silver, clusters containing an odd number of atoms being more reactive than those with an even number.

The coinage metals, both as atoms and clusters, differ in their behaviour towards carbon monoxide because of the values of their  $^2\text{S} \rightarrow ^2\text{D}$  excitation energies, which decrease as  $\text{Ag} > \text{Cu} > \text{Au}$  [22] (Table 2). The stability sequence is determined by the  $5d$  orbital destabilisation, and the spin-orbit coupling in the  $5d_{5/2}$  shell, which assists  $\pi$  back-donation.

### 3.3. Relativistic effects in the chemisorption of carbon monoxide

Notwithstanding the intensive study that carbon monoxide chemisorption has received, certain aspects of the results have proved hard to understand [39–41], and have only recently been illuminated by a recognition of the importance of relativistic effects. Pacchioni et al. [39] have reviewed the uncertainties surrounding the interpretation of results found with the metals of Group 10. They point out that, in analysing valence photoemission spectra, (i) it is wrong to conclude that the stabilisation of the  $5\sigma$  with respect to the  $1\pi$  level is *not* primarily deter-

mined by  $\sigma$  donation; (ii) that changes in surface dipole moments owe more to polarisation effects than to the change carried by the molecule; and (iii) that the assignment of adsorption site on the basis of vibration frequencies is in doubt because shifts of frequency with coverage may be substantially due to dipole–dipole coupling. These authors identify respects in which the molecule’s chemisorption on platinum differs from that on nickel and palladium: they focus on (i) the larger differential shift in frequency between the on-top and bridge sites, and (ii) the smaller change in work function of the metal.

Highly accurate density functional calculations, involving gradient corrections to the exchange–correlation functional and scalar relativistic effects, on carbon monoxide chemisorbed on on-top and bridge sites of the (100) surface of each Group 10 metal show that the different behaviour of platinum in the on-top position is caused by a relativistic contraction of the Pt–CO bond length: this is caused by reduction of kinetic energy repulsion by the mass–velocity corrections. The effect is less at the bridge site, and with palladium [37]: it is absent with nickel. The calculations are claimed to ‘reproduce in a satisfactory way the general features of metal–CO bonding’, which are not found in the absence of the relativistic factor. This substantial and important paper [39] merits serious attention.

Relativistic effects perhaps appear more prominently when the behaviour of the Group 11 metals in carbon monoxide chemisorption is considered. As noted above, the bonding is much weaker than in Group 10, and there are major differences between the three metals: all reports agree, however, that the sequence of adsorption strengths is  $\text{Cu} > \text{Au} > \text{Ag}$ . This is confirmed by a survey of published adsorption enthalpies measured at low coverage [38], by the interpretation of photoemission spectra [42], and by a detailed study of the adsorbed states by direct core and valence photoemission, X-ray absorption and auto-ionisation of core excited



states [43]. Vibration shifts of the  $2125\text{ cm}^{-1}$  band with coverage on films deposited at 4 K have been carefully analysed [44]: they are the resultant of two opposing effects which are separable by the use of  $^{13}\text{CO}$ . A ‘chemical’ or ‘static’ shift arises from changes induced by neighbouring molecules, and this dominates over a ‘vibrational’ or ‘dynamic’ interaction of a direct electromagnetic nature: this vibrational coupling always leads to an *increase* in frequency with coverage. The results obtained (Table 5) give further clear evidence for the egregious behaviour of silver, and the importance of relativistic effects.

Much attention has recently been paid to the chemisorption of carbon monoxide on gold because of the high activity of certain supported gold catalysts in its oxidation [17]. With unsupported gold, chemisorption is most easily detectable on surfaces created at low temperature [44] or on the stepped (332) surface of a single crystal [45]: with supported gold, much depends on the nature of the support and the particle size [17].

The behaviour of the Group 11 metals in carbon monoxide chemisorption has been explained [42] in a similar way to that used for complexes and clusters. In the absence of vacant  $d$  orbitals on the metal, charge donation from them to the  $2\pi$  orbital of the molecule is essential for bond formation: since the  $d$ -band in silver is some  $190\text{ kJ mol}^{-1}$  higher than the  $d$ -bands in copper and gold, energetic overlap with the  $2\pi$  orbital of adsorbed carbon monox-

ide is more favourable for charge exchange with the last two metals.

The performance of metals in catalysing reactions of carbon monoxide naturally depends upon the manner of its chemisorption [46]: this is briefly reviewed in Section 5.3.

## 4. Coordination and chemisorption of hydrocarbons

### 4.1. Introduction

Just as a fruitful correspondence has been seen between carbonyl complexes and clusters, and the chemisorption of carbon monoxide on surfaces, so also have useful correlations been observed between organometallic complexes containing hydrocarbon ligands and the reactions of hydrocarbons with metal surfaces [47–51]. The principal difference lies in the complexity: while the carbon monoxide molecule can assume at most four or five forms, we have to contend with a large number of different hydrocarbon types — linear, branched and cyclic alkenes, alkynes, alkadienes and aromatics, amongst others — each of which can adopt several, sometimes many, forms in complexes or on surfaces. The field enjoys a very large literature [16,23,47–50,52–55], but there are many observations that still await rationalisation. It is only possible now to select a limited area having relevance to catalysis for further examination: attention will be centred on ethene as ligand and adsorbate, for which ample information exists.

### 4.2. Coordination of unsaturated hydrocarbons

Complexes in which a hydrocarbon radical (alkyl or aryl) is purely  $\sigma$ -bonded are known for a number of the metals of Groups 8–11, but are usually unstable unless the  $\beta$ -position is blocked (as with aryl radicals) or absent (as with the methyl ligand) to prevent hydride transfer and elimination of an alkene. The presence of other

Table 5  
Chemical (static) and vibrational (dynamic) shifts in the  $\text{C}\equiv\text{O}$  vibrational frequency on films of the Group 11 metals formed at 4 K [44]

Metal	Chemical shift ( $\text{cm}^{-1}$ )	Vibrational shift ( $\text{cm}^{-1}$ )	Net shift ( $\text{cm}^{-1}$ )
Cu	–21	+21	0
Ag	–34	+12	–22
Au	–30	+17	–13

ligands often stabilises the M–C  $\sigma$ -bond. Stable mononuclear complexes of Au<sup>I</sup> and Au<sup>III</sup> of the forms respectively of RAuL and R<sub>2</sub>AuX (R = alkyl, L = ligand, X = halide) are known, although corresponding complexes of copper and silver are not [16,23].

Alkyl complexes have little relevance to the present exercise, and complexes formed by  $\pi$ -bonding are of much greater interest. Hydrocarbon species may be attached to metal atoms or ions either by a  $\sigma$ -bond or a  $\pi$ -bond or by both or by some combination of the two. Monoalkenes bond to metal atoms and ions in a way which is very similar to that of carbon monoxide, namely by donation of  $\pi$ -electrons into a vacant metal hybrid orbital, if available, ( $\sigma$  component) and by back-donation from an occupied metal  $d$ -orbital into the  $2\pi$  antibonding orbital of the alkene ( $\pi$  component). The extent to which these two processes operate depends upon the nature of the metal, on its oxidation state, on the nature of other ligands and on the kind of substituents (if any) on the alkene. When the metal has no low-lying vacant orbitals, the structure resembles that of a metallocyclopropane, and the alkene changes its geometry to resemble that of an alkane, i.e., the C–C bond stretches and the molecule becomes markedly non-planar. When a major  $\sigma$ -component is present, the same changes occur to a smaller extent, and stronger bonding results [16,23]. Zeise's salt (K[Pt<sup>II</sup>Cl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]) is the archetypal  $\pi$ -alkene complex, the bonding in which has been discussed in great detail [53], while complexes of the type Pt<sup>0</sup>P<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>) (P = trialkylphosphine) are models for the metallocyclopropane form (see below). The bonding observed in practice may lie anywhere between these two extremes.

Alkenes form complexes with both metal atoms and ions. With Pt<sup>II</sup>, Pd<sup>II</sup>, Rh<sup>I</sup>, and some other ions the structure is as in Zeise's salt, i.e., the C–C bond axis is at right angles to the plane of the complex, and the alkene can rotate freely with an activation energy of between 40 and 65 kJ mol<sup>-1</sup>. Complexes are also known for

Pt<sup>0</sup>, Pd<sup>0</sup>, Ir<sup>I</sup>, etc., having the formula MP<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>) (P = phosphine ligand) and a flattened tetrahedral structure: here the alkene cannot rotate because the  $\pi$ -bonding dominates [53]. The importance of oxidation state is also seen in Group 11, where alkene complexes of zero-valent metals are not known, but complexes with Cu<sup>I</sup> and Ag<sup>I</sup> are stable and of some use in the analytical and preparative separation of alkenes. Complexes of Ag<sup>I</sup> with alkenes have been particularly well studied: the proton resonances are de-shielded, unlike the situation with Cu<sup>I</sup> and Au<sup>I</sup> [52]. Alkene complexes of Cu<sup>I</sup> are readily formed, and some with Au<sup>I</sup> are also known [17,23].

Somewhat unstable complexes of Pt<sup>II</sup> and Pd<sup>II</sup> in which two ethene molecules are coordinated to the same atom are known, the Pd complex only being stable under ethene [54]. A bicycloheptene (B) complex of Ni<sup>0</sup> (NiB<sub>3</sub>) is also known, and very unstable complexes of the form Ni(C<sub>2</sub>H<sub>4</sub>)<sub>m</sub> ( $m = 1-3$ ) [56] and Ni<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)<sub>n</sub> ( $n = 1,2$ ) [57] have been studied by matrix isolation methods. Unstable molecules of this type may also provide clues as to the forms that are reactive in catalysis at higher temperatures.

Alkenes containing a C–H group adjacent to the double bond form complexes by loss of an H atom and the formation of a  $\pi$ -allylic radical in which electrons are delocalised over three carbon atoms. Many such complexes are known, especially with palladium [54] and nickel [16]. Dienes form complexes by coordination of both double bonds, particularly stable complexes being formed with cyclic dienes. Diene complexes are stabler than those with mono-enes, because both bonds must be broken simultaneously to disrupt them. This has been clearly shown by the inhibition of alkene isomerisation by dienes in the presence of aqueous Rh<sup>I</sup>: this effect can be used to estimate the relative strengths of the coordinations, the dienes being 10<sup>2</sup>–10<sup>3</sup> times more strongly held than the alkene [58]. Alkynes behave similarly. Some alkyne complexes analogous to those formed by alkenes (i.e., involv-

ing only one  $\pi$ -bond) are known, but the greater number of C–M bonds that can be made allows other structures to be formed: in binuclear complexes for example the alkyne generally sits across the M–M bond. Complexes involving benzene and the cyclopentadienyl ion with metal atoms are well known and understood [16,23].

#### 4.3. Chemisorption of unsaturated hydrocarbons on metals

If the chemistry of organometallic complexes involving hydrocarbons seems difficult, that of hydrocarbon species at metal surfaces assumes a daunting complexity, and defies easy summary. The structures encountered, as identified by LEED and various spectroscopies [47–51], constitute an “organometallic zoo”, the existence of which has been recognised for more than three decades [58–61]. The greater variety of species in comparison with those found in complexes arises from the availability of larger ensembles of metal atoms, so that more bonds to a surface can be formed; and also H atoms can be more easily removed because they can be accommodated elsewhere. It is again necessary to focus on those observations which seem to have relevance to catalysis, and to ignore almost entirely the complex processes by which the first-formed species at low temperature decompose on heating to give ultimately carbon [47–49,62].

There is a reason for adopting this restriction, additional to the simplification that it brings. It seems likely that species formed abundantly at low temperature may resemble those formed at high coverage at higher temperatures, after decomposition products have covered much of the surface, and that these weakly bonded species are those that are most catalytically reactive. This argument is well illustrated by the evidence that  $\pi$ -bonded ethene is often formed at low temperature, and that it decomposes on heating, usually via the  $\sigma$ -diadsorbed form, and often giving ethylidyne, which is unreactive in hydrogenation, while the weakly held  $\pi$  form

appears to be the most easily hydrogenated species. This statement summarises much experimental work, fully discussed in several reviews and papers [49,50], which must be referred to for further detail.

Identification of the structure of adsorbed species has been greatly facilitated by studies using single crystal surfaces, because the kind of structure formed is somewhat dependent on surface geometry: under given conditions one structure often predominates, so that there is now a good basis for understanding the site requirements or preferences for each structure, and for using this information to analyse the more complicated case of small supported particles, where several kinds of surface site are expected to co-exist. The use of vibrational spectroscopies (FTIR, HREELS) and structure-determining techniques (LEED, NEXAFS) has led to the recognition of two principal, perhaps extreme, types of structure, namely (i)  $\sigma$ -diadsorbed (or  $\mu_2$ - $\eta^2$ ), where the alkene carbons have effectively rehybridised to  $sp^3$  and two C–M  $\sigma$ -bonds are formed, giving Sheppard's Type I spectrum, and (ii)  $\pi$ -adsorbed (or  $\eta^2$ ), giving the Type II spectrum closely resembling the structure in Zeise's salt. The unique complex  $(C_2H_4)Os_2(CO)_8$  is a model for the former. A third form, denoted as  $\pi\sigma$ -adsorbed (also  $\eta^2$ ), is the metallocyclopropane structure, giving Type I' spectrum, for which the complex  $(C_2H_4)Os(CO)_4$  is a model [47–50]. The apparent failure of ruthenium to form the binuclear ethene complex may be a further manifestation of the relativistic effect.

The C–C bond order in the  $\pi$ -adsorbed species is variable, depending on the extents of the donor and acceptor processes, and moreover at least two of these forms can co-exist since the energy differences are not great, so that speciation can be a major problem. On the basis of differences in the IR spectra, a “ $\pi\sigma$ -parameter” taking values between zero and unity has been evaluated, zero representing the free molecule and unity the single C–C bond as in  $C_2H_4Br_2$  [47,48,63,64]. Alternatively, and perhaps better,

Table 6

Values of the  $\pi\sigma$  factor [63,64] and of the C–C bond order [50,65] for chemisorbed ethene on various metal surfaces

The  $\pi\sigma$  factor is given first; it takes values between 0 and 1: the C–C bond order comes second; it takes values between 1 and 2.

The  $\pi\sigma$  factor for Zeise's salt  $K[PtCl_3(C_2H_4)]$  is 0.38; for  $[Ag(C_2H_4)]BF_4$ , 0.12. Similar values, probably more accurate, are given by  $C_2D_4$ .

O...M represents presorbed partial monolayer of O atoms.

Group 8		Group 9		Group 10		Group 11	
Fe(110)	0.55/1.20	–	–	Ni(111)	0.80/1.33	Cu(100)	0.21/1.66
Fe(111)	0.86	–	–	Ni(100)	0.83/1.41	Cu <sup>a</sup>	0.19
Ru(001)	0.85/1.35	Rh(111)	0.50/1.39	Pd(100)	0.78 <sup>b</sup> /1.38	Ag film	–/1.88
O...Ru(001)	0.42	Rh(100)	0.55/1.16	Pd(111)	0.43/1.61	O...Ag(100)	0.14
–	–	–	–	O...Pd(100)	0.30	Ag <sup>a</sup>	0.09
–	–	–	–	Pt(111)	0.92/1.13	Au <sup>a</sup>	0.25
–	–	–	–	Pt(210)	–/1.67	–	–

<sup>a</sup>Determined by SERS on metal foil.

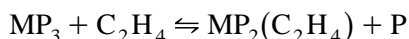
<sup>b</sup>The value for the  $\sigma$ -diadsorbed form; the value for the  $\pi$  form is 0.30.

a bond order value may be derived from the bond length estimated directly from LEED measurements [47,48,65]: representative values of both parameters are given in Table 6. Higher alkenes appear to behave in much the same way as ethene [47,48]. Extensive spectroscopic and structural work has been done on alkynes, especially ethyne [47–49] and more limited work on dienes [47–49,66] and arenes, especially benzene [67–69].

An early simple-minded attempt [58] to construct models for chemisorbed hydrocarbon structures by analogy with coordinated molecules, and assuming a molecular orbital picture on the surface based on an unchanged termination of bulk structure “was not well received”, but has, nevertheless, been of some use [50]. Unfortunately it only applies to fcc metals, and its extension to other crystal structures has proved difficult.

#### 4.4. Evidence for relativistic effects in unsaturated hydrocarbon complexes

Within the elements of Group 10, there is experimental and theoretical evidence that complexes formed by palladium are less strong and stable than those of nickel and platinum [54]. Equilibrium constants for the equilibrium



have been measured for  $P = PPh_3$  in benzene at 298 K, giving values for nickel ( $\sim 300$ ), palladium (0.013) and platinum (0.122) [70]. XRD and NMR data have been reported for the solid complexes  $MP_2(C_2H_4)$  ( $M = Ni, Pt; P = PPh_3$ ): an unstable  $PtP_2(C_2H_4)_2$  exists in solution [71]. The non-local quasi-relativistic DF method has been applied to a number of ethene and ethyne complexes, viz.  $MP_2(C_2H_4)$ ,  $MP_2(C_2H_2)$  and  $M(CO)_4(C_2H_4)$  ( $P = PPh_3$ ), with results shown in Table 7: the hydrocarbon ligand is taken to be sideways-on, giving a square-planar structure. Without the relativistic factor, bonding would weaken progressively with increasing  $Z$ : its inclusion results in greater back-donation into  $\pi^*$  orbitals, stretching of the C–C bonds, and greater back-bending of the H atoms [72]. Similar calculations have been made for the carbene complexes  $MCH_2^+$  in the ground state: relativistic effects on bond dissociation energies are greatest for platinum and gold [73].

Table 7

Calculated hydrocarbon—M bond energies ( $\text{kJ mol}^{-1}$ ) for ethene and ethyne complexes [72]:  $P = PPh_3$

Metal	$MP_2(C_2H_4)$	$MP_2(C_2H_2)$	$M(CO)_4(C_2H_4)$
Ni	159	189	163
Pd	83	91	128
Pt	88	104	164

There are considerable differences between the stabilities and reactivities of the diphosphine complexes of Pt<sup>II</sup> and Pd<sup>II</sup> [74–76]: thus, PtP<sub>2</sub> (P = PPh<sub>3</sub>) adds hydrogen by oxidative addition at room temperature, but no reaction occurs with PdP<sub>2</sub>, due to the stability of the *d*<sup>10</sup> configuration. Reductive elimination is slow and endothermic with Pt<sup>II</sup>P<sub>2</sub>(H)(CH<sub>3</sub>)<sub>2</sub>, but fast and exothermic with the Pd<sup>II</sup> compound. Pt<sup>II</sup>P<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub> is very stable and does not undergo reductive coupling, while the corresponding Pd<sup>II</sup> compound gives ethane. Pt<sup>II</sup>P<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> does, however, give ethane and ethene by β-hydride transfer, and reductive coupling can also occur with Pt<sup>IV</sup>P<sub>2</sub>Cl<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>.

Of the binuclear gaseous clusters of Group 11, only Cu<sub>2</sub> and Au<sub>2</sub> react with ethene, the process being faster and more exothermic with the latter [22].

#### 4.5. Evidence for relativistic effects in hydrocarbon chemisorption

Most of the available relevant evidence concerns the metals of Group 10. The literature creates the clear impression that palladium differs from both nickel and platinum in important ways, specifically in showing a greater tendency to give the π-adsorbed state with ethene. Close inspection of the literature, however, reveals a somewhat complex situation, and some contradictions.

The σ-diadsorbed form of ethene is observed on all metals of Groups 8–10 *except palladium* (cobalt and osmium have not yet been studied) [50]; the π form is seen on all faces of palladium at low temperatures [47,48], from which it either desorbs unchanged ((111) face [77]) or decomposes at 333K ((110) face [69]) or possibly converts directly to ethylidyne ((111) face [47,48]). However, on the (100) surface both σ and π forms are found, the “πσ” factors being respectively 0.78 and 0.30 (Table 6 [63]). In general, palladium resembles the metals of Group 11 in giving chiefly the π form of ethene

at low temperature, due perhaps to the free atom (to which surface atoms approximate) having a closed *d*-shell [47,48]. The importance of surface geometry is also evident in the case of platinum, where, although the diadsorbed form is often seen, the π-form appears on reconstructed and stepped surfaces [50]. The π-form is also facilitated by partial coverage of surfaces by oxygen or carbon atoms; with the latter a site-blocking mechanism may operate, eliminating sites of sufficient size to form the σ-diadsorbed state.

Attempts have been made to correlate the preferred chemisorbed structure with various physical attributes of the metal, such as the theoretical ‘interstitial electron density’ and sublimation enthalpy [50], but there is insufficient experimental evidence to establish such relations, and moreover, as noted above, the dependence of the observed forms on surface geometry renders such simplistic connections of doubtful value. What is potentially far more profitable is to use the identity of the chemisorbed forms as a quantitative probe of surface structure. Thus, for example, at a step on a platinum surface, electron density is thought to be low above it, and high below it, so that the former site may tend to accept the σ-diadsorbed form and the latter the π form [50]. More quantitative spectroscopic information is however needed before progress in this direction can be made. These considerations also suggest that small metal particles may be able to exhibit different forms at the same time, which complicates not only the interpretation of vibrational spectra [47,48] but also the construction of reaction mechanisms.

Ethyne chemisorbed on palladium surfaces undergoes a number of interesting reactions: reversible chemisorption, reversible C–H bond-breaking, hydrogenation to ethene, and conversion to benzene and carbon [69]. Hydrogenation and trimerisation occur most readily on the (111) face, less on the (100) and hardly at all on the (110). This last reaction has also been observed on Ni(111) (but not with platinum),

and recalls the Reppe chemistry in which nickel complexes also form oligomers with ethyne (see below). 1,3-Butadiene adsorbs as the di- $\pi$  form on palladium but as the mono- $\sigma$  form on platinum [66].

A striking example of the difference between these two metals is provided by the recent account of the behaviour of cyclohexene adsorbed on their (111) faces [78]. In its conversion to benzene, a tightly-bond  $C_6H_9$  intermediate is formed only on platinum: interaction of frontier orbitals, chiefly  $\pi$  on the hydrocarbon and  $d$ -band on the metal, is much stronger with platinum. Relativistic augmented-plane-wave calculations have shown the palladium  $d$ -band to have the lower energy, and therefore overlap with the hydrocarbon's  $\pi$  orbitals is poorer.

#### 4.6. Relativistic effects in the coordination of hydrogen

Hydrogen and other simple molecules coordinate to metal atoms in complexes and are chemisorbed by metal surfaces. It is unnecessary to review this field, which is already well served by its literature [25,79–81]: one or two features do, however, highlight the importance of relativistic effects in this area.

Iron, ruthenium and osmium form complexes of the type  $MP_3H_4$ . The four H atoms are coplanar with one of the phosphorus atoms; with osmium there are four separated H atoms, but with the other metals there are two H ligands and one  $H_2$  molecule, which can act as a  $\sigma^*$  acceptor via its antibonding vacant  $\sigma^*$  orbital [82]. Calculations using “a current DF method at the NL-SCF + QR level with non-local and quasi-relativistic corrections included self-consistently” account for this difference. The changeover is a result of now familiar destabilisation of the  $5d$  orbitals, making osmium a better donor than the others. Iridium in the  $Ir^V$  state forms a pentahydride  $IrP_2H_5$  in which the hydrogens lie in a planar pentagon, while the protonated form is  $[Ir^{III}P_2H_2(\mu^2-$

$H_2)_2]^+$  [83]: there are no analogous rhodium hydrides.

Gaseous  $Au_2$  clusters react with hydrogen, but  $Cu_2$  and  $Ag_2$  do not [22]; from spectroscopic measurements on  $M_2$  and  $MH$  molecules [84] (Table 2), enthalpies of reaction are estimated as  $-96$ ,  $-4$  and  $-186$   $\text{kJ mol}^{-1}$ , respectively, for copper, silver and gold. There is indirect evidence for a substantial solubility of H atoms in gold [85,86] (but not silver or copper): it is of course much more soluble in palladium (and nickel) than in platinum.

## 5. Relativistic effects in catalysis

### 5.1. Correlations between coordination, chemisorption and catalysis

The foregoing review would be of lesser interest if it did not provide a basis for rationalising a number of observations in the field of catalysis. Connection between coordination and homogeneous catalysis has been the justification for many a research grant application in organometallic chemistry and indeed it is clear that a successful catalysed reaction entails having the reactant(s) coordinated in the appropriate way and not so strongly as to be unreactive. The same principle applies equally in heterogeneous catalysis [79], where it is perhaps better illustrated, as the Volcano Principle; activity passes through a maximum as a factor determining strength of adsorption is increased, i.e., as the chemisorption complex or transition state passes from being too unstable to being too stable. The main outlines of these correlations were already clearly visible 35 years ago [58], and have not changed significantly with the passing years. We may now, therefore, briefly look at the broad features of homogeneous and heterogeneous catalysis to see how the trends in coordination and chemisorption behaviour which are influenced by relativistic effects are reflected in reactivity patterns.

## 5.2. Relativistic effects in homogeneous catalysis

At one level this subject might be dismissed in a single sentence: *almost all homogeneously catalysed reactions and metal-mediated reactions of organic molecules involve compounds or complexes containing an element in Groups 8–10 of the first or second Transition Series* (we are not concerned here with other Groups except 11). The remainder of this section will illustrate this generalisation, the continuing validity of which is confirmed by the list of contents of almost any issue of *J. Mol. Cat. A: Chem.*, or the appropriate ‘Highlights’ section of *Chemistry and Industry*.

Early successes with homogeneous hydrogenation involved  $\text{Fe}(\text{CO})_5$ , the  $\text{Co}^{\text{II}}(\text{CN})_5^{3-}$  ion and compounds of  $\text{Ru}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Ag}^{\text{I}}$ . A very notable advance was made with the discovery of Wilkinson’s complex  $\text{Rh}^{\text{I}}\text{P}_3\text{Cl}$ , which paved the way for asymmetric hydrogenation using chiral ligands [23]. This complex is very specific for terminal alkenes, the bulky phosphine groups inhibiting formation of a secondary alkyl group from internal alkenes: with deuterium, only dideuteroalkanes are formed [23].  $\text{Rh}^{\text{I}}$  in aqueous solution, however, catalyses double-bond migration in alkenes [58]; this reaction also occurs in a chromatographic column when  $\text{Rh}^{\text{I}}$  in 1,2-dihydroxyethane is used as the stationary phase [87]. Platinum and iridium compounds are rarely cited as homogeneous hydrogenation catalysts, although the  $\text{PtCl}_2\text{—SnCl}_2$  complex in aqueous solution also catalyses alkene isomerisation: it is, however, poor for hydrogenation [88].

A few organometallic complexes (e.g.,  $\text{Ru}_3(\text{CO})_{12}$ ) catalyse Fischer–Tropsch synthesis [89], and syngas is converted to methanol by cobalt and rhodium compounds. These elements are of course those used for hydroformylation, the latter replacing the former because it affords higher yields of primary aldehydes [23,90]: the rhodium-catalysed process is one of the major accomplishments of homogeneous catalysis by

metal complexes. Water–gas shift is catalysed by iron and ruthenium carbonyl complexes.

Complexes of  $\text{Ni}^{\text{II}}$  catalyse the oligomerisation of unsaturated hydrocarbons. Reppe discovered the conversion of ethyne to benzene or cyclo-octatetraene [16], while the name of Wilke is associated with the dimerisation of alkenes by  $\text{NiX}(\pi\text{-allyl})$  ( $\text{X} = \text{halide}$ ) with  $\text{AlCl}_3$ ;  $\text{Rh}^{\text{I}}$  complexes are also effective for the latter reaction [23]. Complexes of the type  $\text{MX}_2\text{N}_2$  ( $\text{M} = \text{Ni}, \text{Pd}$ ;  $\text{N}_2$  a bidentate nitrogen-containing ligand) and  $\text{MX}_2\text{N}_3$  ( $\text{M} = \text{Fe}$ ;  $\text{N}_3$  a tridentate ligand) together with methylaluminoxane as co-catalyst effect the polymerisation of ethene either to  $\alpha$ -alkenes or to high-density polyethylene, depending on the nature of alkyl substituents on the phenyl groups attached to the nitrogens [91]. It is a fair bet that analogous cobalt, rhodium and ruthenium complexes would act similarly.

A second major industrial success for homogeneous catalysis is the Wacker process, namely the oxidation of ethene to ethanol by nucleophilic attack of  $\text{OH}^-$  catalysed by  $\text{Pd}^{\text{II}}$ , with a copper salt to facilitate the re-oxidation of  $\text{Pd}^{\text{0}}$  to  $\text{Pd}^{\text{II}}$  [16,92]: in the presence of acetic acid the product is the commercially important vinyl acetate (ethenyl ethanoate). Zeise’s salt is slowly hydrolysed to ethanol, this having been the inspiration for Wacker chemistry.

Carbonylation of methanol to acetic (ethanoic) acid catalysed by carbonyls of iron, cobalt and nickel in the presence of an iodine source was also discovered by Reppe [16]: the industrial process subsequently used  $\text{Rh}^{\text{I}}\text{COI}$  [93], but rhodium is now being superseded by iridium [94] with ruthenium as promoter [95].

The only significant use of a platinum compound in homogeneous catalysis is hydrosilylation, i.e., the addition  $\text{HSiR}_3$  to an alkene, giving usually a terminal silane [23]. It seems likely that the stabler alkene complex formed by  $\text{Pt}^{\text{II}}$  is needed here, otherwise the bulky  $-\text{SiR}_3$  group would displace it and reaction could not occur.

Also largely absent from this catalogue are the Group 11 metals, whose complexes with

carbon monoxide and with unsaturated hydrocarbons are generally too unstable to participate in catalysis. Those of the 5d elements (Ir,Pt) are usually *too* stable (except as noted above). Complexes showing the necessary moderate stability are, therefore, those of the first and second Transition Series elements, of which palladium, rhodium and nickel appear most often. The exact location of maximum activity depends upon the nature of the reaction and the other ligands present. There is clearly an analogue of the Volcano Principle of heterogeneous catalysis at work [58], but the lack of quantitative information on reaction kinetics on more than a very few reactions makes detailed analysis of the relevant factors difficult.

### 5.3. Relativistic effects in heterogeneous catalysis

Correspondence between coordination and chemisorption on the one hand, and between homogeneous and heterogeneous catalysis on the other, has been exhaustively explored, and the similarities that have been found are impressive [58]. To some extent they are unaffected by oxidation state, i.e., complexes of Pt<sup>0</sup>, of Pt<sup>II</sup> and those formed on platinum surfaces containing atoms in a variety of coordinations are all recognisably connected. However, there are several factors which render heterogeneous catalysts different from, and more useful than, their homogeneous counterparts. (i) The presence of an extended surface, even such as there may be on particles containing only 12–15 atoms [96], enlarges the number of possible chemisorbed forms, and provides adjacent sites for other reactants. (ii) A surface can easily be modified by promoters and selective poisons. (iii) Heterogeneous catalysts can if necessary be used at temperatures inaccessible to homogeneous catalysts. Keeping these differences well in mind, we may now seek evidence in heterogeneously-catalysed reactions for the operation of relativistic effects.

Reactions of syngas on metals of Groups 8–11 have been thoroughly researched, but findings are not easy to summarise as so much depends on reaction conditions (temperature, pressure, metal dispersion, etc). All the metals of Groups 8–10, and copper, are active: the Fischer–Tropsch reaction, giving higher alkenes, alkanes and oxygenated products, depending on conditions, is possible on iron, cobalt, nickel, ruthenium and osmium. Ruthenium is very apt to give high molecular-weight hydrocarbons under high pressure. Copper and palladium can form methanol, and rhodium can make C<sub>2</sub> oxygenated products. Under certain conditions, all metals of Groups 8–10 can give methanation. Recent work has indicated that gold may have some use in reactions of syngas [17], but silver has not yet shown useful activity. It is clear that metals which do not form simple carbonyls (palladium, platinum, copper) can, nevertheless, chemisorb carbon monoxide and catalyse its hydrogenation.

All the metals of Groups 8–10 are active for the hydrogenation of unsaturated hydrocarbons: the activity of copper and gold [17] is of a lower order, but is none the less measurable. We focus now on the behaviour of the small linear alkenes, alkadienes and alkynes, and on palladium and platinum, where major differences in behaviour, attributable to a relativistic effect, are clearly seen [25,97].

In this family of reactions, selectivity can be shown in a number of ways. (i) In the reaction of an alkene with deuterium, the exchanged alkene, in which some of the H atoms have been substituted for D, may be returned to the gas phase, as well as alkanes containing both H and D atoms. (ii) Alkenes containing four or more carbon atoms can undergo double-bond migration and *E–Z* isomerisation, the changed reactant appearing in the gas phase as well as the alkane. (iii) Alkynes and alkadienes may be reduced selectively to an intermediate alkene, which appears alongside the final product alkane. (iv) Substituted alkynes afford various alkenes, but that formed by *Z*-addition of two H



atoms to the triple bond is most preferred. (v) Alkadienes can give various alkenes, e.g., butadiene can give all of the butene isomers.

It consistently appears, with all manner of reactants and types of catalyst, that palladium is much superior to platinum in allowing the return of intermediate products to the gas phase [25,97]. With alkynes and alkadienes, palladium (which is much the more active) affords alkenes in selectivities which approach 100%, *Z*-2-butene being the main product from 2-butyne and 1-butene from 1,3-butadiene. Platinum is much less selective. In the reactions of alkenes, exchanged and isomerised alkenes are often the principal products. Reaction mechanisms on palladium have been formulated with  $\pi$ -allylic intermediates, while those on platinum employ  $\sigma$ -bonded species [25]. Analysis of the products formed on hydrogenation of isoprene (2-methyl-1,3-butadiene) gives a clear indication of the role of  $\pi$ -allylic species [98].

It was long ago appreciated that these results implied that alkenic species were less strongly chemisorbed on palladium than on platinum [97], and that this paralleled the stabilities of alkene  $\pi$ -complexes. Similarly, the invocation of  $\pi$ -allylic species in palladium-catalysed reactions followed from the commonly-found analogues in complexes. The base metals (iron, cobalt, nickel and copper) can also give high selectivities and efficient alkene exchange; ruthenium and rhodium are somewhat less selective, while osmium and particularly iridium are least selective [25,97]. The foregoing considerations also account for the long-standing use of nickel catalysts for fat hardening [79], and the more recent acceptance of palladium as an alternative [99]. As elsewhere, the relativistic effect is most clearly visible in Group 10, but is also operative in Groups 8, 9 and 11. It is a further deduction that intermediates in these reactions must be at least partly  $\pi$ -bonded in order to account for the electronic effects observed.

Both palladium and platinum have, however, low activity in alkane hydrogenolysis [79], much

less than that of the base metals and of Groups 8 and 9: it is, nevertheless, greater than that shown by the Group 11 metals. The outstanding difference between them is that platinum in a bifunctional catalyst achieves the reactions of petroleum reforming via alkenes which migrate to and from the acidic function: palladium cannot, although both can effect skeletal isomerisation in monofunctional systems. The reasons for palladium's disability are not much discussed (it is more interesting to discuss why a metal is active than why it is inactive); one possibility is that it may too easily dehydrogenate excessively, giving dienes which readily polymerise and lead to carbon deposition. The similarity of the activities of the two metals in hydrogenolysis is due to the absence of  $\pi$ -bonded intermediates in the key stages of the mechanism.

Readers may wish to consider for themselves whether there is evidence for relativistic effects in the many other reactions of hydrocarbons (alkane exchange, dehydrogenation ...) which there is no time to consider here. They may also play an important role in the many kinds of reactions catalysed by gold [17].

## 6. Relativistic effects in other chemical and catalytic phenomena

It is possible that relativistic effects may operate in areas where its role is as yet unrecognised; possible subjects for future attention might be the following. (i) Heavy metal allergy: platinumosis is well-documented, but palladium compounds are harmless. (ii) Heavy metal chemotherapy [6]: platinum complexes seem to be the most useful [100,101]. (iii) Use of gold compounds in treatment of arthritis [101]. (iv) Heavy metal toxicity. (v) The role of bismuth and antimony in comparison with arsenic in oxidation catalysis, and of tin in comparison with germanium in this field and also in alloys with platinum for hydrocarbon transformations.

## 7. Conclusions

The final question has to be: does it really matter that the effects of Special Relativity underlie trends and differences in coordination, chemisorption and catalysis? In one sense, no: awareness of them will not help us to make better catalysts, and many of the observations noted have been interpreted to a certain depth by non-relativistic theories and concepts which give qualitatively correct answers in terms of ionisation potentials, energies of electron bands and levels, etc. [55]. Many workers have been aware of the stabilisation of *s* and *p* orbitals relative to *d* orbitals, and of related ionisation potential differences, before the fundamental contribution of relativity to these effects became clear [102]. The first mention of relativity in stabilising the 6*s* electrons does, however, date from the late 1960s [103].

In compiling this review, it has proved very difficult to locate much of the quantitative information on for example bond strengths and enthalpies of formation of organometallic complexes on which proper comparisons could be based. It appears that experimental thermochemistry is a dead subject, and that it is now easier to compute the answer than to measure it. Similarly with homogeneous catalysis: there is a large literature comprising qualitative statements, but except for one or two of the simpler reactions there do not appear to have been many proper kinetic investigations by physical chemists. Although surface science and heterogeneous catalysis enjoys a much more quantitative foundation, recent reviews [47–51] nevertheless, are somewhat of a catalogue of observations for which the unifying theoretical framework has not yet emerged.

A further hindrance to the construction of a review such as this is the near-total neglect of the findings of surface science in inorganic chemistry texts.

The concept does, however, succeed in unifying a range of phenomena concerning the chemistry of the elements and their compounds, with

particular reference to the stability and reactivity of carbonyl complexes and of coordinated hydrocarbons, which in turn connect with and illuminate our understanding of reactions of these molecules in homogeneous and heterogeneous catalysis. This review is little more than a partial ‘shopping list’ of areas to which further theoretical attention is required, and to which the importance of Special Relativity has not yet been considered. Therefore, in another sense, the answer to the question whether it matters must be yes: the fundamental duty of the scientist is *rerum cognoscere causas* — to know the causes of things. And it is interesting to realise that, whenever we touch an item containing gold or tin or lead, we are in contact with the effects of something of truly cosmic importance.

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