

New Studies in Fullerene Chemistry

SOME RUSSIAN PLATINUM METALS FULLERENES RESEARCH

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Studies on fullerene chemistry carried out in the Laboratory of Organometallic Stereochemistry at INEOS, Moscow, are briefly reported. These include work with platinum metals complexes, in particular, on novel methods of preparing η^1 fullerene (C_{60} and C_{70}) complexes of platinum, palladium, rhodium and iridium. A new approach is the use of mercury-platinum bimetallic compounds, $R-Hg-PtL_2-X$, as a source of the PtL_2 moiety to be transferred onto a (6:6) double bond in fullerenes. Bis(aryl)platinum(II) complexes can react similarly. Other products of this reaction are discussed. The first optically active organometallic fullerenes of the type $C_nM(+)$ DIOP, where $n = 60$ or 70 , have also been prepared and the circular dichroism spectra investigated. In addition, the molecular structures for $C_{60}Pd(PPh_3)_2$ and $C_{60}Pt(+)$ DIOP have been solved. Higher catalytic activity for the hydrogenation of a triple to a double bond has been observed with $C_{60}Pd(PPh_3)_2$ adsorbed on porous carbon than with palladium/porous carbon.

The stability of the giant carbon cluster C_{60} was first predicted by quantum chemical calculations in the 1970s (1, 2), but the actual existence of both C_{60} and C_{70} in carbon vapour was not discovered until 1985, when it was detected by mass spectrometry (3), and resulted in the award of the Nobel Prize for Chemistry in 1996 to Curl, Kroto and Smalley.

However, for chemical study, fullerenes only became available in multigram quantities five years later, after the development of the carbon arc burning method (4). The study of fullerenes is interdisciplinary, as they have relevance, for example, to: solid state physics, spectroscopy, chemistry, materials science, astrophysics, life sciences and geology.

As chemical entities fullerenes are different from other forms of carbon, such as diamond, graphite, or linear carbon, in that they constitute a whole family of isolated individual molecules rather than a continuous polymeric system. From a chemical point of view, fullerenes can be regarded as highly unsaturated, strained alkenes, with an unusual three-dimensional structure, made exclusively of carbon, and as

such they have attracted a lot of attention in terms of their general reactivity – in particular as ligands for transition metals.

This latter field of study was initiated by the work of Fagan, Calabrese and Malone who described the first platinum η^3 -bonded C_{60} complex (5). Shortly afterwards we reported that the structures of the fullerenes permit them, in principle, to act as ligands of different hapticity, continuously from η^1 to η^6 (6). One aspect that has been of great interest to us is that chirality may occur in doubly metallated exohedral complexes when the two metal groups are identical: in η^6, η^6-C_{60} and in η^6, η^6-C_{70} , η^6, η^3-C_{70} and η^5, η^3-C_{70} (7). Both pentahapto- and hexahapto-metal complexes are well-known in platinum metals chemistry (as shown for instance, by metallocenes and arene-metal complexes). However, in fullerene chemistry, only η^3 -ligated metal complexes had been reported until 1996, when the synthesis of η^5 metal derivatives of X_2C_{60} with a partly broken fullerene structure was reported (8).

Recently, this Journal published a survey of some current results in the area of fullerenes

The Electrochemistry of (η^2 -C ₆₀)Pd(PPh ₃) ₂							
Compound	Reductive wave potentials, - E _{1/2(redu)} , volts						
C ₆₀	0.34		0.78		1.30	1.78	2.30
C ₆₀ Pd(PPh ₃) ₂	0.34	0.57	0.78	0.99	1.27	1.47	
C ₆₀ Pd(PPh ₃) ₂ + Pd(PPh ₃) ₄		0.57	0.81	0.99	1.25	1.48	
$2 \text{ C}_{60}\text{Pd}(\text{PPh}_3)_2 \leftrightarrow \text{C}_{60}[\text{Pd}(\text{PPh}_3)_2]_2 + \text{C}_{60}$ $\text{C}_{60}\text{Pd}(\text{PPh}_3)_2 \leftrightarrow \text{C}_{60}\text{Pd}(\text{PPh}_3) + \text{PPh}_3$							

bonded to the platinum group metals (9) in which one paper of the present authors was referred to. However, there is other work on this topic published by our group, which has largely gone unreported in the review literature (10). Therefore, we would like to take this opportunity of briefly outlining our results.

Topics in fullerene chemistry in which we are interested include:

- (i) the synthesis, molecular structure and reactivity of C₆₀ and C₇₀ co-ordinated to the platinum group metals;
- (ii) the formation and reactivity of Z-fullerenyl free radicals, where group Z is linked to the fullerene through the magnetic nucleus (such as ³¹P, ¹⁰B-¹¹B, ¹⁹⁵Pt, etc.) for study by ESR (electron spin resonance) spectroscopy;
- (iii) optically active organometallic fullerene derivatives.

Synthesis of Fullerenes with Platinum and Palladium

The synthesis and molecular structures of palladium fullerene complexes have been reported by us (11). X-ray investigations have revealed that distortions of the fullerene cores in both platinum and palladium η^2 -C₆₀M(PPh₃)₂ complexes are very similar (11). The most interesting feature of these complexes is their square planar – rather than tetrahedral – arrangement of four ligated atoms around the metal. This is different from Pt(0) and Pd(0) complexes with normal alkenes, such as ethylene, but similar to those with electron-withdrawing alkenes, such as tetrafluoroethylene or tetracyanoethylene.

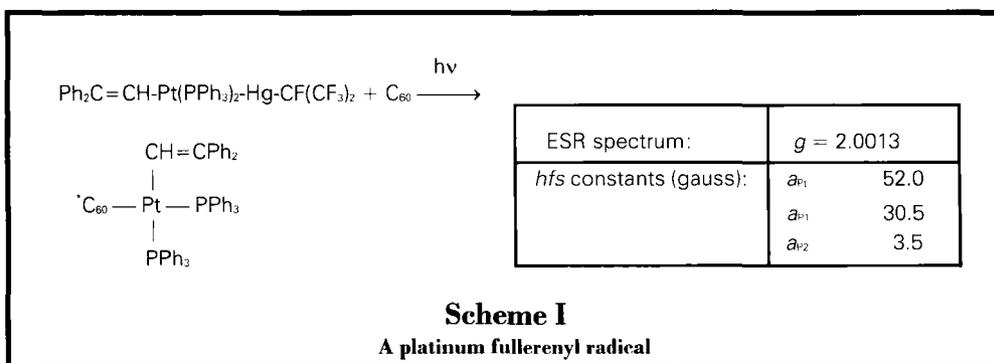
This suggests that essential electron transfer occurs from the metal to the fullerene core. The X-ray structure of a related, optically active, platinum fullerene complex has also been solved (*vide infra*).

An electrochemical study of η^2 -C₆₀Pd(PPh₃)₂ in acetonitrile in the presence of an excess of either Pd(PPh₃)₄ or PPh₃ revealed the disappearance of some reductive waves common to free C₆₀, see the Table, above (12). This was interpreted to mean the existence of the following equilibrium:



without phosphine ligand dissociation.

We have found a novel, alternative method for the preparation of platinum fullerene complexes using mercury-platinum compounds of general formula R-Hg-PtL₂-X as a source of the PtL₂ moiety (13). The synthesis of this group of mercury-platinum organobimetallic compounds was previously developed by us; it involves the insertion of Pt(0) carbenoids into the mercury-element bond (Hg-X), where the element X may be halogen, carbon or a metal and R is an organyl group (14). The important structural feature of these organobimetallics is a *cis*-arrangement of two phosphine ligands (L) around the platinum atom. The stability of these mercury-platinum compounds has been known to depend strongly on the nature of groups R and X. It was found that their reactivity, versus fullerenes, may be different as a consequence. Thus, if only common groups, such as halogen, aryl or alkyl are present in the molecule, then Pt(PPh₃)₂ is



transferred smoothly onto a fullereryl [6:6] double bond.

However, when R is the electron-withdrawing perfluoroalkyl group, homolysis of the metal-metal bond occurs selectively, leaving the platinum-carbon bond intact. Initially a platinum-centred free radical is formed which immediately attaches to the fullerene to give a relatively stable platinum fullereryl radical, observable by ESR at room temperature (13), see Scheme I. Its structure is explained by the ESR spectrum, where hyperfine splitting (*hfs*) is observed due to one platinum (^{195}Pt) and two non-equivalent phosphorus (^{31}P) nuclei. This shows that the *cis*-arrangement of the two phosphine ligands is preserved in this novel radical species.

Strangely enough, no stable η^1 -platinum fullereryl derivative has been reported previously, and the above-mentioned free radical is the only representative of monohapto-platinum-fullereryl compounds.

The above-mentioned approach was successfully used for the synthesis of $\eta^2\text{-C}_{70}\text{Pt}(\text{PPh}_3)_2$, see Scheme II, with the formation of two isomers being identified by the ^{31}P NMR spectrum. The major isomer exhibited an AB system (a pair of doublets) that corresponds to addition on the most strained *a-b* bond near the pole of the ellipsoid. The minor isomer exhibited one singlet that pointed unambiguously to the equivalence of both phosphorus atoms. This can happen if the addition occurs on the *c-c* bond (the *c-c* bond is more removed from the pole and is bisected by the plane of symmetry) (15).

Recently it was found that C_{60} can even react

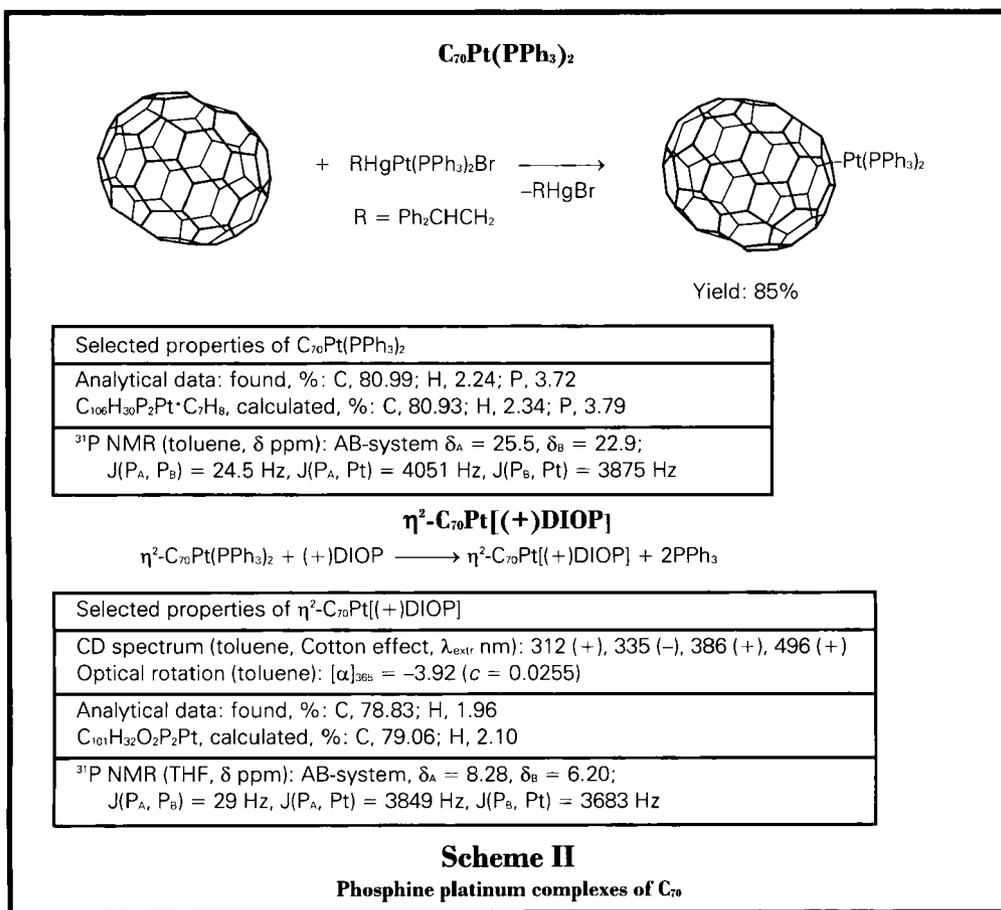
with bis-organylplatinum complexes, Ar_2PtL_2 , where Ar = *p*-tolyl, again to give $\eta^2\text{-C}_{60}\text{Pt}(\text{PPh}_3)_2$ and biaryls (16). The reaction appeared to proceed as a concerted process with initial coordination between the platinum atom and the double bond.

Formation and Reactivity of Z-Fullereryl Free Radicals

Fullerenes themselves are known readily to add many kinds of free radicals (17). We have studied the behaviour of $\eta^2\text{-C}_{60}\text{M}(\text{PPh}_3)_2$ during the reaction with free dialkoxyphosphoryl radicals, $(\text{AlkO})_2\text{P}(\text{O})^*$. Several low intensity ESR signals were observed in addition to the parent $^*\text{C}_{60}\text{P}(\text{O})(\text{OAlk})_2$ signal, which indicates that there is a preferred attack on the metal followed by immediate demetallation to give the latter.

An indirect approach, based on the metallation of the radical dimer, was used to prepare η^2 -platinated fullereryl radicals, see Scheme III. Because the fullerene-fullerene bond in this dimer is very weak (*ca.* 10 kcal mol $^{-1}$) it can be broken by irradiation with red, visible light (630–680 nm). In fact, five distinguishable ESR signals have been observed, each with different *g*-factors and *hfs* constants, *a*, (due to coupling to phosphorus) which can be assigned to the regioisomers of η^2 -platinated phosphoryl-fullereryl radicals (18).

The reactions of C_{60} and C_{70} with the complexes, $\text{HM}(\text{CO})(\text{PPh}_3)_3$, M = rhodium or iridium, occur with high regio- and stereo-selectivity by the replacement of one PPh_3 ligand to



give η² metal derivatives on the [6:6] bonds. With C₇₀, the double bond located on the sharp end of its ellipsoid is involved. A related diene-

hydride complex, HIr(COD)(PPh₃)₂, reacts in a similar way (19). The interaction of photolytically generated

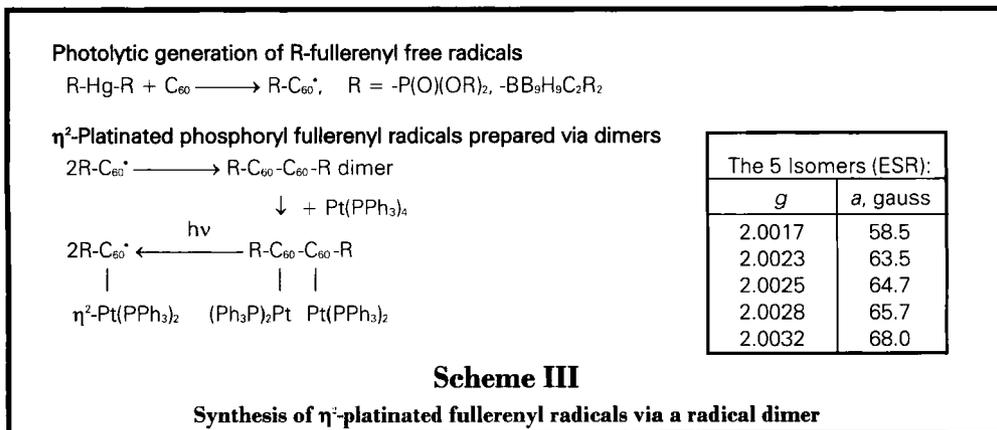
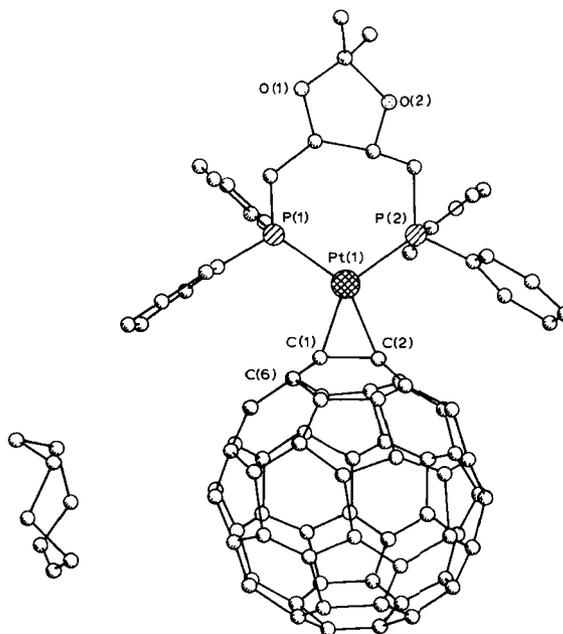


Fig. 1 Molecular structure of the enantiomeric platinum fullerene complex

Bond	Bond length, Å
Pt(1)-C(1)	2.09
Pt(1)-C(2)	2.12
Pt(1)-P(1)	2.28
Pt(1)-P(2)	2.26
C(1)-C(2)	1.51
C(1)-C(6)	1.44
Angle	Angle, deg
C(1)-Pt(1)-C(2)	42.0
C(1)-Pt(1)-P(1)	104.2
C(2)-Pt(1)-P(2)	104.4
P(1)-Pt(1)-P(2)	109.5



(*vide supra*) dialkoxyphosphoryl radicals with the iridium fullerene complexes, $\eta^2\text{-C}_{60}\text{IrH}(\text{Y})\text{-PPh}_3$, where $\text{Y} = (\text{CO})(\text{PPh}_3)$ or (COD) , at room temperature, was found to result in partial demetallation (attack on the metal) and addition (attack on the fullerene core) to give three isomeric phosphoryl(iridium)fullerenyl radicals, which have:

- 1 $g = 2.0026$, $a_r = 66.7$ gauss;
- 2 $g = 2.0037$, $a_r = 64.25$ gauss;
- 3 $g = 2.0027$, $a_r = 59.25$ gauss

with the species 1 being strongly predominant. The parent phosphorylfullerenyl radical, $^*\text{C}_{60}\text{P}(\text{O})(\text{OAlk})_2$, with $g = 2.0023$, $a_r = 63.5$ gauss, formed more slowly from the iridium complex compared with that from the platinum analogue (20).

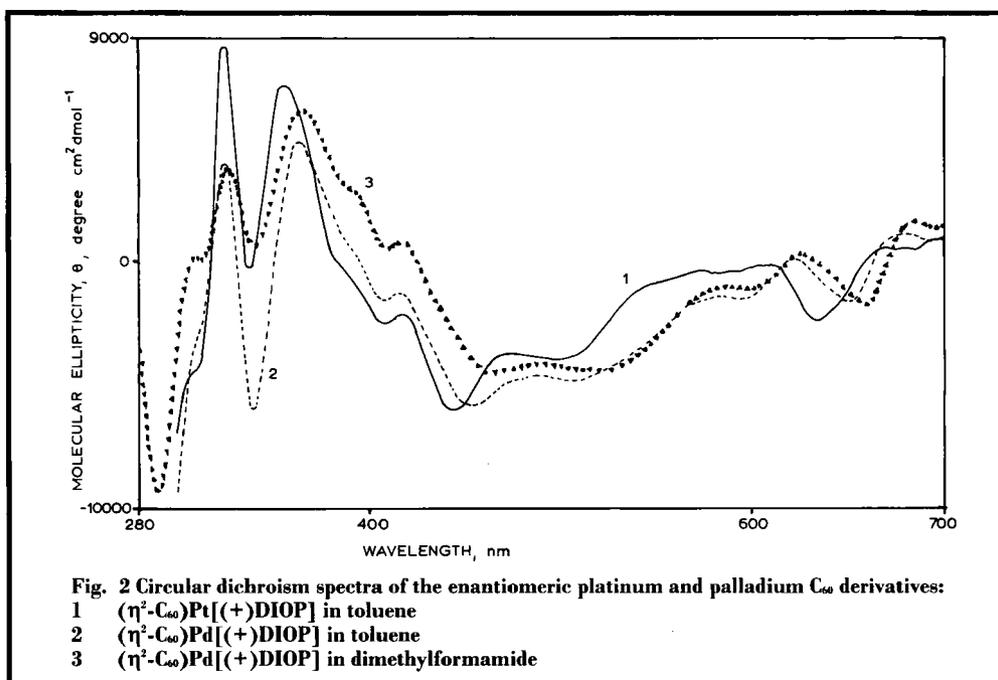
Optically Active Organometallic Fullerene Derivatives

One of our main objectives has been the synthesis of optically active organometallic fullerene derivatives. These are interesting both in themselves and as the possible precursors for asym-

metric catalysts for use in various organic reactions. Additionally, as some platinum complexes are known to possess biological activity, this can be also expected for the platinum fullerenes. Thus, optically active compounds could be of interest in different fields, in part they have potential as materials for non-linear optics. Added to this, the circular dichroism of these compounds can provide information about the electronic transitions in the fullerene core.

The first optically active *organic* derivatives of fullerene have been reported by Vasella, Diederich and colleagues (21). These are sugar-fullerene derivatives whose circular dichroism spectra were recorded, and exhibited many Cotton effects due to the electronic transitions in C_{60} itself.

We took advantage of the opportunity to introduce optically active ligands at the metal atom in η^2 -fullerene metal complexes and thus synthesise the palladium (22) and platinum (23) C_{60} complexes bearing the (+)DIOP ligand: [(+)-2,3-isopropylidene-2,3-*trans*-dihydroxy-1,4-bis(diphenylphosphino)butane] at the metal. These were the very first optically active



organometallic fullerenes to be reported. They were prepared either by exchanging the triphenylphosphine ligand for (+)DIOP, see Scheme II, or by direct synthesis from the fullerene, the diphosphine ligand, and the dibenzylideneacetone complex, $Pd_2(dba)_3$:



The molecular structure of the enantiomeric platinum fullerene complex was determined by X-ray study of the solvate with one molecule of *cis*-cyclooctene, see Figure 1, isolated after recrystallisation of the compound from a *cis*-cyclooctene-hexane mixture. The inclusion of *cis*-cyclooctene appeared to be absolutely necessary for the growth of good quality single crystals, but in spite of this, the solvate molecule had no close contacts with the fullerene molecule (23). Similar (+)DIOP complexes have also been prepared from C_{70} .

Circular dichroism spectra were measured in toluene and in dimethylformamide, and several Cotton effects were found (unpublished results) which could be unambiguously attributed to the electronic transitions in the fullerene core, see

Figure 2. In some cases the Cotton effects may be shifted due to interaction with the metal. In general, the wavelengths of the Cotton effects are close to those reported in (21).

Finally, we have observed the catalytic effect of $C_{60}Pd(PPh_3)_2$ adsorbed on a porous carbon (sibunite) for the selective hydrogenation of a triple bond in 3,7-dimethyloctaene-6-yne-1-ol-3 to a double bond in 3,7-dimethyloctadiene-1,6-ol-3 (linalool). This occurred more efficiently than with metallic palladium adsorbed on the same carrier under the same conditions (24). There is no possibility of asymmetric catalysis in this case, nonetheless there is a chance that the optically active fullerene palladium analogue would be a useful asymmetric catalyst for other hydrogenations which might result in chiral products.

Acknowledgement

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Oxygen Dissociative Adsorption on Platinum Surfaces

The chemical and physical processes occurring between gases and solids during surface catalysis are under continuous investigation and revision. Since platinum metals find wide use as catalysts, and readily chemisorb molecules and dissociate bonds, the interaction between platinum and oxygen was selected for detailed study. Surface kinetics of a heterogeneous reaction are usually described by the Langmuir model, which assumes that free adsorption sites on a surface are randomly occupied.

Now, however, scientists at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin have observed that oxygen dissociation is affected by nearby chemisorbed species (T. Zambelli, J. V. Barth, J. Wintterlin and G. Ertl, *Nature*, 1997, **390**, (6659), 495–497). Using a platinum(111) surface, the distribution of chemisorbed oxygen was recorded by scanning tunnelling microscopy, at intervals from 160 down to 50 K, after exposure to 10^{-6} torr s oxygen. At 160 K the O atom coverage first formed randomly distributed adatom pairs, then as tem-

peratures were lowered, the pairs formed clusters, which grew into quasi-one dimensional chains, 10 to 50 Å long, with branches at 120° angles. The chains formed an irregular network, followed by the appearance of triangular O clusters at the points where three chains met. The clusters had inhomogeneous distribution alongside large areas of bare platinum. Finally, triangular islands protruded from the surface.

It is assumed that there is a mobile adsorbed molecular precursor state, which is trapped and dissociated by already adsorbed O atoms – the active sites. At lower temperatures the precursor lifetime and its mean free path increase, giving it a higher probability of reaching an O atom. It is suggested that dissociation of the precursors is highest at the ends of the chains.

This apparent increased local reactivity and modification of the electronic properties near chemisorbed particles is an important finding for the general description of catalytic reaction kinetics, and has relevance for most high temperature and pressure industrial heterogeneous catalyses.