PHYSICAL ORGANOMETALLIC
CHEMISTRY VOLUME 3

Unusual Structures and Physical Properties in Organometallic Chemistry

Edited by
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Free University of Brussels, Belgium
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Free University of Brussels, Belgium
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Physical Organometallic Chemistry

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Series Preface

Physical organic chemistry, the study of the basic physical principles of organic reactions, is not a new field: in 1940, Hammett had already written a book with this title. This area has developed during the last 20 years mainly because of the explosive growth of sophisticated analytical instrumentation and computational techniques, going from the simple Hückel molecular orbital theory to *ab initio* calculations of increasing accuracy enabled by the advent of fast supercomputers.

An analogous genesis characterized physical organometallic chemistry. Understanding the basis of chemical reactivity and the detailed pathways of reactions of organometallic compounds is now one of the major goals of physical organometallic chemists. Correlation of structure with reactivity, increasing in sophistication, contributes powerfully to the understanding of electronic transmission, as well as of steric and conformational properties, including solvent effects. Homogeneous catalysis has reached a development stage making it a wide, complex topic deserving special consideration. Chiral induction is also becoming increasingly important, considering the economic importance of asymmetric syntheses in the design of pharmaceuticals: organometallic compounds play a key role in this area; understanding this role is the key to further progress.

Accordingly, the major developments of physical organometallic chemistry are not only relevant to *ab initio* calculations of metal-based organic compounds or new spectroscopic tools like multidimensional high-resolution NMR. They also involve new ingenious technologies to study reaction mechanisms, group-theoretical approaches to investigate the fluxionality of organometallic molecules, photochemical reactions on organometallic substrates, and, last but not least, experimental highlights like unstable organometallic compounds in matrices, piezochemistry, and sonochemistry.

The main goal of this series 'Physical Organometallic Chemistry' is to offer to post-graduates and researchers leading contributions written by well-known scientists reviewing the state-of-the-art of hot topics animating this wide research area, in order to develop new insights and to promote novel interest and investigations.

Preface

The term 'unusual' is often misused in chemistry with the purpose of (over?)-emphasizing structural or property originality of novel chemical compounds. Organometallic chemistry does not escape from this trend, but paradoxically, suffers also from the insufficient scientific exploitation of really unusual techniques, tools, properties or parameters to investigate really unusual chemical features or structures. This can be traced to a vast extent to a quite traditional, albeit respectable, strategy of conducting research in organometallic chemistry consisting basically of a classical scheme involving sequentially synthesis, purification, basic characterization, structure determination by X-ray diffraction, and, if any, chemical applications in synthesis or catalysis. Apart maybe from X-ray diffraction, the characterization tools remain often at routine level, e.g. in proton and carbon-13 NMR or IR spectroscopy, elemental analysis and mass spectrometry, with the identity of chemical structures in crystalline and solution states being taken too often for granted. In this way other properties—electronic, magnetic, fluxional—are sometimes overlooked or insufficiently addressed. Starting from this standpoint, the idea came up to conceive a book offering a selection of unusual properties, tools or structures that could serve as a source of new challenges in broader fields of organometallic chemistry than those in which they have been presently created, implemented or applied.

This present book is intended for a vast majority of scientists working in various areas of organometallic chemistry. This statement looks trivial at first glance, but is less so when considering the ever-increasing speed of development of novel physical methods and the diversity of their real or potential applications to organometallic chemistry, even though, as stated above, they are not widespread. Actually, it becomes more and more difficult to keep track in exploiting the full potential of these methods, especially when unusual structures or physical properties are concerned. Hence, the principal idea of this book is to offer in this particular context a *Capita Selecta* of unconventional and thought-provoking topics in organometallic chemistry, presented by experts in each field at state-of-the-art level. As intended in this book, this approach leads either to reviews covering a specific uncommon class of organometallic compounds or to overviews which relate uncommon physical properties with various classes of organometallic compounds. Thus, extended cross-linking of useful information is provided, even for people working in rather different areas of organometallic chemistry. Clearly, it is not possible to

cover the theme of such a book in an exhaustive manner. However, the *Capita Selecta* offered are representative of this original approach and serve as examples which should stimulate the reader to consider one or other physical method or structural pattern for his own special interests. He/she should also find unusual structural features for systems, apparently not related to his own field, which however possess familiar physical data. In this way, this book should help the reader to understand relevant physical data in a more general way. The text is streamlined into two main axes, namely unusual properties reflecting structures and bonding situations, on the one hand, and uncommon structural features or structure–reactivity relationships, on the other hand. The first axis consists of six chapters: the electrochemistry–structure relationship in transition metal carbonyl clusters with interstitial atoms, with special emphasis on the contrast between carbides and nitrides; unusual nuclear shielding and coupling constants in organometallic compounds, with contrast between data of unusual bonding situations and data from the basic simple chemical molecules involved; deuterium relaxation times and quadrupolar coupling constants in metal hydrides and metal–dihydrogen complexes in solution; novel aspects of solid-state NMR spectroscopy of organometallic compounds; Mössbauer spectroscopy addressing metal atom motions in iron organometallics; magnetic communication and spin equilibria of organometallic complexes, and spin transitions in binuclear organometallic complexes. The second axis consists of four contributions: molecular clusters with facial arene ligands; cobaltafulvenes and cobaltapentalenes, as highly polar metallic π-systems with unusual properties; highly nucleophilic ylidic ligands for the preparation of unusually stable metal complexes; supramolecular interactions in solid organo-antimony and -bismuth chemistry.

In this way, it is hoped to provide of a broad overview of unusual techniques, research tools, structures and properties that can stimulate novel research axes in areas of organometallic chemistry where they have never previously been addressed.

1 Structure and Electrochemistry of Transition Metal Carbonyl Clusters with Interstitial or Semi-Interstitial Atoms: Contrast between Nitrides or Phosphides and Carbides

PIERO ZANELLO

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Transition-metal carbonyl clusters containing *interstitial* or *semi-interstitial* atoms have been the subject of many studies, particularly in view of the fact that the insertion of interstitial atoms inside the metal cage of the clusters often increases the number of valence electrons (hence affecting to some extent the reactivity), leaving essentially unaltered the molecular geometry with respect to the original species. Their preparative [1,2], structural [1,2], spectroscopic (NMR) [3] and theoretical [4] aspects have been elucidated and their possible use as catalysts has been proposed [5]. In addition, their electrochemical behaviour has been mostly reviewed in a series of articles devoted to a systematic examination of the electrochemical behaviour of homo- [6] and hetero-metal [7] carbonyl clusters.

In this present paper, we should like to focus more specifically on the different, and in some cases contrasting, electrochemical behaviour of *homoleptic* transition-metal carbonyl clusters containing interstitial or exposed *N, P* atoms with respect to the *C*-containing analogues. Since these nitride or phosphide carbonyl clusters can be considered as a link between *organometallic* and *coordination* compounds, it is hoped that a detailed comparison of their redox aptitude can help theoreticians in understanding more and more the extent to which the nature of such interstitial heteroatoms might affect the electron mobility inside such compounds.

We will examine here only those complexes for which the X-ray structures have been solved—discussions of the structural details are given in the relevant literature references, or mostly in References [5] and [6]. Even if in many cases there are not sufficient electrochemical data to allow comparisons to be made

between *nitride/phosphide*-containing metal clusters and their *carbide* analogues, we think it is useful to give literature references to the X-ray structures of all of the complexes known so far.

The molecular structures and electrochemical responses presented here are adapted from the original figures quoted in the text. Unless otherwise specified, all the electrode potentials are referred to the saturated-calomel electrode.

1   INTRODUCTION

Although *carbide*-containing transition-metal carbonyl clusters have been known for a long time [1,2], delays were experienced before electrochemists began to deal with them, so that their redox chemistry was adequately, although roughly explored by chemical routes. In fact, the use of chemical reagents does not allow the redox properties of a molecule to be finely tuned. For instance, Chini's group in Milan pioneeringly investigated not only the synthetic and structural aspects of metal clusters, but also their redox chemistry. Thus, one can find in the literature the structural characterization of a few redox couples of metal carbonyl clusters obtained 'blindly' by using chemical reagents. In this connection, Figures 1–3 show the molecular
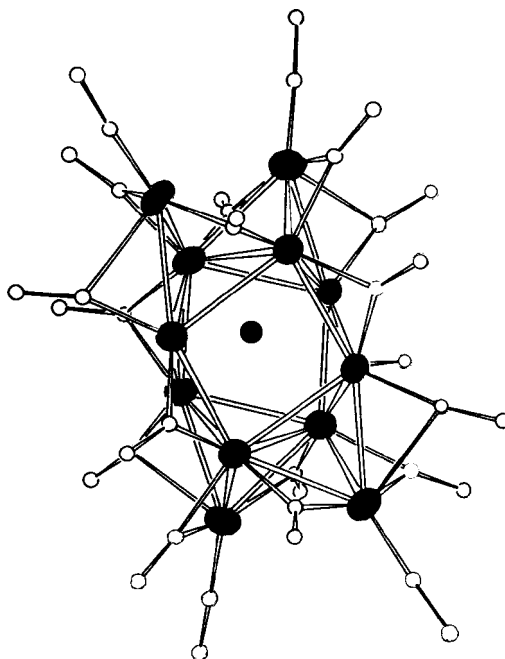
Figure 1   Molecular structure of the tetraanion $[Co_3Ni_9(C)(CO)_{20}]^{3-}$
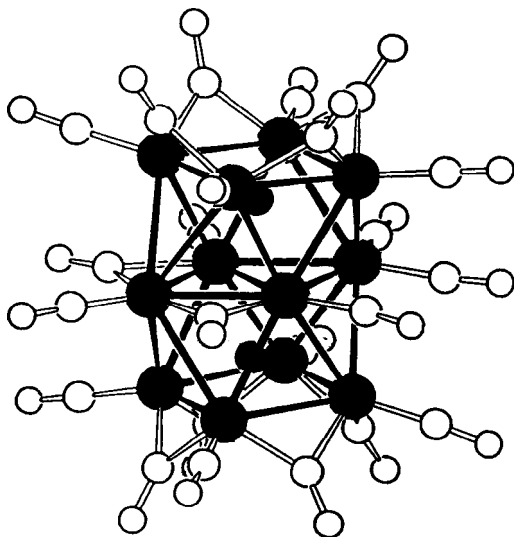
Figure 2 Molecular structure of the trianion $[Rh_{12}(C)_2(CO)_{23}]^{4-}$
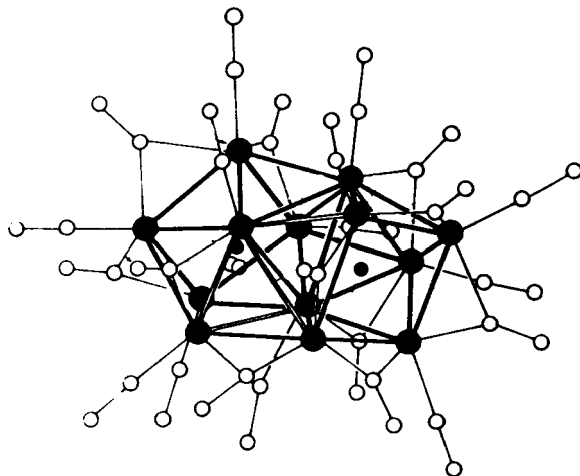
Figure 3 Molecular structure of the tetraanion $[Co_{13}(C)_2(CO)_{24}]^{4-}$

structures of one member of each of the couples, $[Co_3Ni_9(C)(CO)_{20}]^{3-/2-}$ [8,9], $[Rh_{12}(C)_2(CO)_{23}]^{4-/3-}$ [10,11], and $[Co_{13}(C)_2(CO)_{24}]^{4-/3-}$ [12,13].

In all of these cases, the redox congeners are isostructural with each other and only minor variations in the metal–metal, metal–carbon(carbonyl), and metal–carbon(carbide) bonding distances occur upon addition/removal of one electron.

As previously mentioned, the use of chemical reagents does not allow the multiple redox states of a molecule to be adequately determined. For instance, $[Co_3Ni_9(C)(CO)_{20}]^{3-}$ not only undergoes the chemically reversible one-electron removal process, $[Co_3Ni_9(C)(CO)_{20}]^{3-/2-}$ ($E^{0'} = -0.30$ V), but it is also able to add two electrons in a single step ($E^{0'} = -1.71$ V), affording the pentaanion $[Co_3Ni_9(C)(CO)_{20}]^{5-}$, which, however, is a transient species ($t_{1/2} \approx 1$ s) (Figure 4) [14].

Analogously, the chemical picture concerned with the redox change $[Rh_{12}(C)_2(CO)_{23}]^{4-/3-}$ appears to be correct as far as the full stability within the family is concerned. Indeed, as Figure 5 illustrates [5], the redox ability is more extended in that $[Rh_{12}(C)_2(CO)_{23}]^{4-}$ not only undergoes reversibly the cited one-electron oxidation ($E^{0'} = -0.46$ V), but also exhibits a second irreversible one-electron removal ($E_p = -0.16$ V), as well as a single two-electron reduction to the corresponding hexaanion $[Rh_{12}(C)_2(CO)_{23}]^{6-}$ ($E^{0'} = -1.62$ V), which, however, is relatively short-lived ($t_{1/2} \approx 1$ s).

Figure 4 Cyclic voltammogram recorded at a platinum electrode for a Me$_2$CO solution containing $[Co_3Ni_9(C)(CO)_{20}]^{3-}$ (scan rate, 0.2 V s^{-1})

Figure 5 Cyclic voltammetric response exhibited by $[Rh_{12}(C)_2(CO)_{23}]^{4-}$ in MeCN solution, with a platinum working electrode (scan rate, 0.2 V s^{-1})

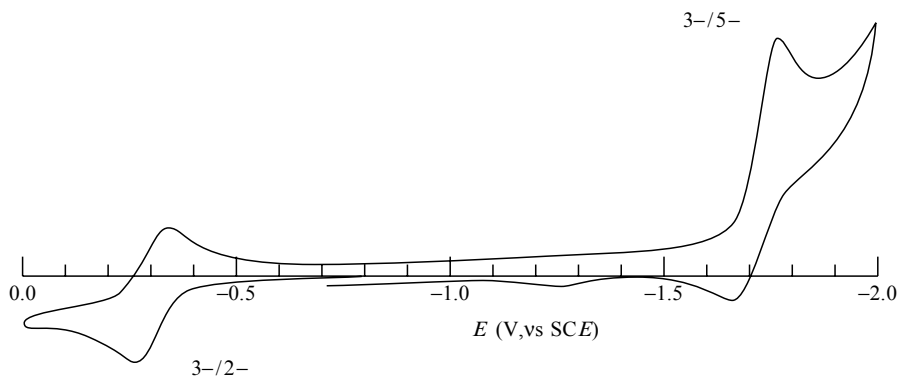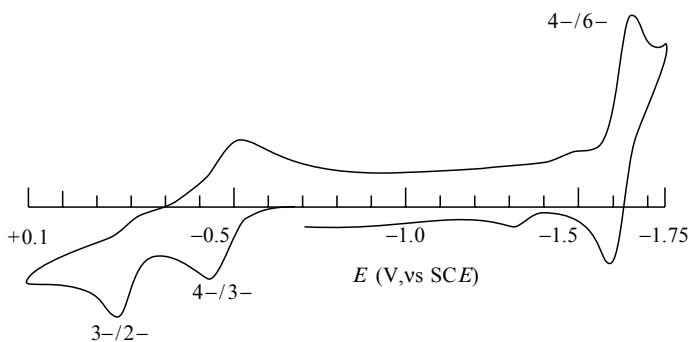Even more instructive is the case of the redox family of $[Co_{13}(C)_2(CO)_{24}]^{4-}$. As Figure 6 proves, the tetraanion not only undergoes reversible the cited one-electron oxidation to the trianion $[Co_{13}(C)_2(CO)_{24}]^{3-}$ ($E^{0'} = -0.54$ V), but it also exhibits the chemically reversible sequential access to the corresponding penta- ($E^{0'} = -1.06$ V) and hexa- ($E^{0'} = -1.68$ V) anions, $[Co_{13}(C)_2(CO)_{24}]^{5-/6-}$, respectively [5].

Furthermore, the usefulness of electrochemical studies in the present field is not limited to the discovery of multiple, stable or unstable, redox states of clusters, but also to the eventual conversion of a molecule to a somewhat related species by simple redox processes [15].

For instance, the dianion $[Ru_6(C)(CO)_{16}]^{2-}$, the octahedral geometry of which is shown in Figure 7(a) [16] undergoes an irreversible two-electron oxidation ($E_p = +0.48$ V, vs Ag/AgCl) to the neutral more carbonylated congener $Ru_6(C)(CO)_{17}$, which in turn undergoes an irreversible reduction ($E_p = -0.47$ V) (Figure 7(b)) [17].

As confirmation, $Ru_6(C)(CO)_{17}$, the octahedral geometry of which is shown in Figure 8(a) [18], exhibits a quite complementary voltammetric response (Figure 8(b)), thus pointing out that, upon two-electron addition, it converts again to the decarbonylated dianion $[Ru_6(C)(CO)_{16}]^{2-}$ [17].

By way of comparison, the isostructural and isoelectronic non-carbide dianion $[Ru_6(CO)_{18}]^{2-}$ (Figure 9) [19] also exhibits in dichloromethane solution a two-electron oxidation coupled to fast chemical complicated behaviour, although this it occurs at a notably lower potential value ($E_p = -0.36$ V, vs Ag/AgCl) [20].

Finally, as an alternative to the thermally induced phosphine substitution, which affords a series of not easily separable products, the anodic oxidation of
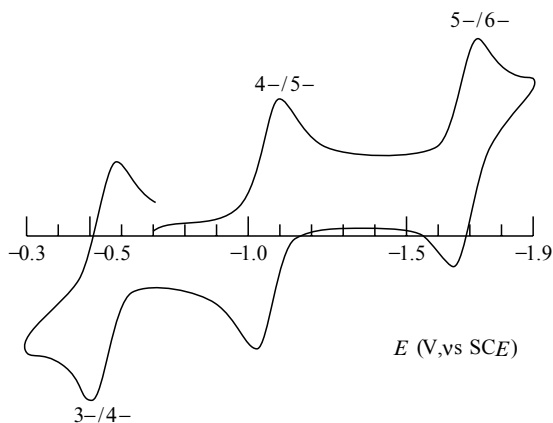

Figure 6 Cyclic voltammetric response exhibited by $[Co_{13}(C)_2(CO)_{24}]^{4-}$ in MeCN solution, with a platinum working electrode (scan rate, 0.2 V s^{-1})

(a)

(b)

2−/0

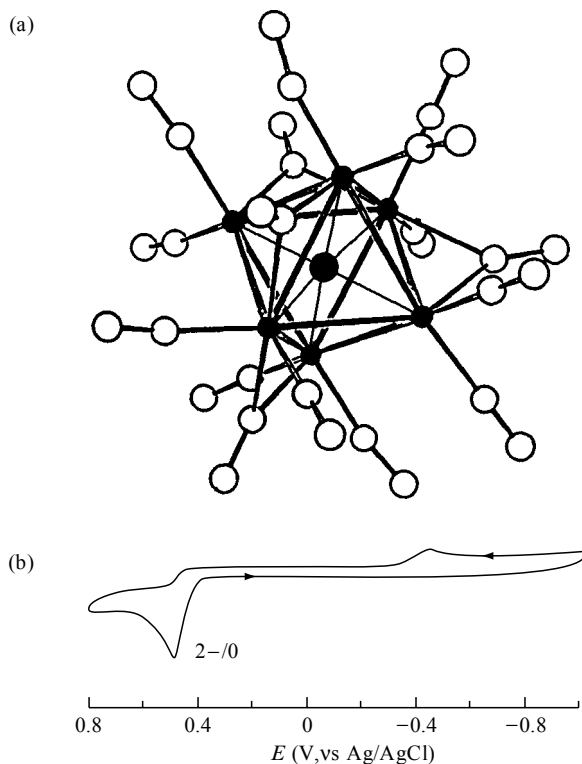0.8   0.4   0   −0.4   −0.8

E (V, vs Ag/AgCl)

Figure 7 (a) Molecular structure of $[Ru_6(C)(CO)_{16}]^{2-}$, and (b) its cyclic voltammetric profile in CH_2Cl_2 solution

$[Ru_6(C)(CO)_{16}]^{2-}$ in the presence of phosphines selectively leads to the mono-substituted neutral species $Ru_6(C)(CO)_{16}(PR_3)$ [17]. In this connection, Figure 10 shows the molecular structure of $Ru_6(C)(CO)_{16}(PPh_2Et)$ [21].

2   HOMONUCLEAR CLUSTERS

2.1   HOMONUCLEAR IRON CLUSTERS

2.1.1 $Fe_4(C)(CO)_{13}$ and $[Fe_4(C)(CO)_{12}]^{2-}$ versus $[Fe_4(N)(CO)_{12}]^-$

As Figure 11 illustrates, the three 62-cluster-valence-electron (CVE) complexes $[Fe_4(C)(CO)_{12}]^{2-}$, $Fe_4(C)(CO)_{13}$ and $[Fe_4(N)(CO)_{12}]^-$ possess a butterfly geometry [22–24].

It has been briefly reported that the dianion $[Fe_4(C)(CO)_{12}]^{2-}$ undergoes, in nonaqueous solvents, four oxidation steps, with only the first two of these having features of transient chemical reversibility [25]. This means that the

(a)

(b)

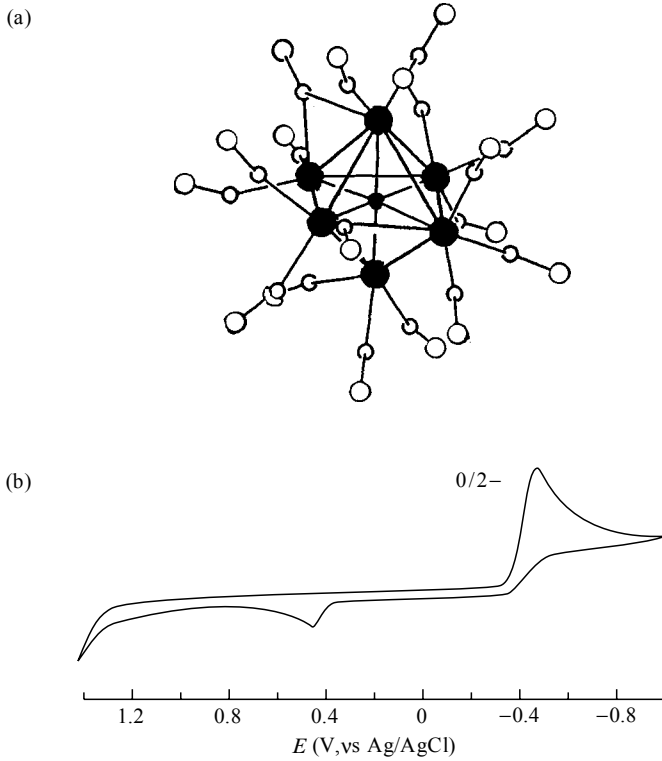0/2−

1.2   0.8   0.4   0   −0.4   −0.8

E (V, vs Ag/AgCl)

Figure 8 (a) Molecular structure of $Ru_6(C)(CO)_{17}$, and (b) its cyclic voltammetric profile in CH_2Cl_2 solution

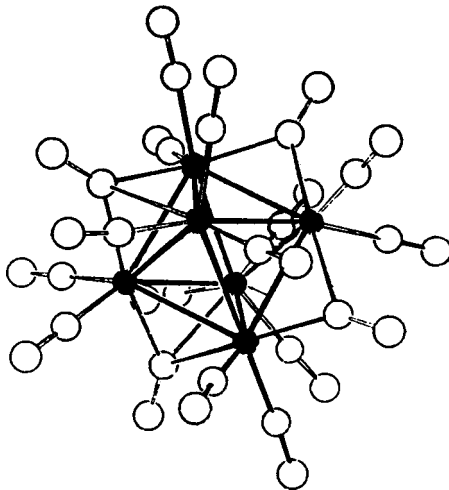**Figure 9** Molecular structure of $[Ru_6(CO)_{18}]^{2-}$

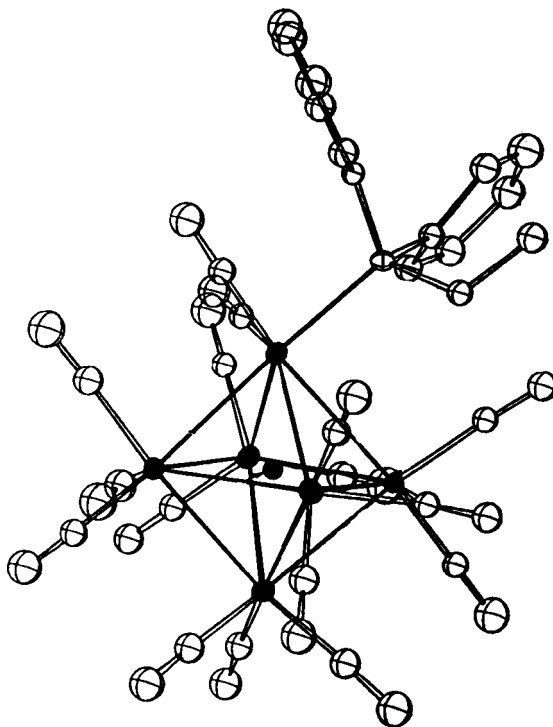**Figure 10**   Molecular structure of $Ru_6(C)(CO)_{16}(PPh_2Et)$

corresponding 61/60-CVE congeners $[Fe_4(C)(CO)_{12}]^{-,0}$ are only partially stable and tend to decompose. As a matter of fact, oxidation under CO atmosphere affords $Fe_4(C)(CO)_{13}$ [26].

Quite opposite is the redox ability of the monoanion $[Fe_4(N)(CO)_{12}]^-$. As Figure 12 shows, this undergoes in acetonitrile solution two sequential one-electron reductions at $E^{0'} = -1.23$ V and -1.58 V, respectively, with both having features of chemical reversibility [27].

Indeed, over the long time-scales of macroelectrolysis only the 63-CVE dianion $[Fe_4(N)(CO)_{12}]^{2-}$ remains quite stable. Furthermore, in the presence of triphenylphosphine, the electrochemical reduction triggers the electrocatalytic substitution of one carbonyl ligand, affording $[Fe_4(N)(CO)_{11}(PPh_3)]^-$ [27]. The electrochemical pathway quite parallels the thermal one, which also allowed the obtainment and consequent structural characterization of $[Fe_4(N)(CO)_{11}(PMe_2Ph)]^-$ [28]. The molecular structures of these substituted complexes are shown in Figure 13. In both cases, the phosphine ligand replaces one carbonyl on the wingtip, i.e. the less coordinated iron vertex of the Fe_4 butterfly.