Russian Chemical Reviews **69** (8) 639 – 660 (2000)
© 2000 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2000v069n08ABEH000577

Synthesis and properties of functionalised dendrimers

I P Beletskaya, A V Chuchurjukin

Contents

I.	Introduction	639
II.	Hydrocarbon dendrimers containing conjugated π-systems	639
III.	Conjugated dendrimers containing transition metal atoms	641
IV.	Dendrimers containing pincer-type ligands and their metal complexes	644
V.	Dendrimers containing transition metal coordination complexes	646
VI.	Dendrimers containing complexes with metal – carbon σ-bonds	652
VII.	Dendrimers containing terminal ferrocenyl groups	653
VIII.	Dendrimers containing transition metal π-complexes	654
IX.	Dendrimers containing central metal-containing fragments	655

Abstract. The published data on the synthesis, structure, properties and applications of dendrimers containing conjugated π-systems, transition metal complexes and organometallic compounds are surveyed and systematised. The bibliography includes 83 references.

I. Introduction

The chemistry of dendritic molecules, which is a fundamentally new branch of chemistry, began to develop explosively in the past few years. The beauty of these flower- or star-shaped structures is so amazing that it may spark the imagination of artists. However, apart from the great attractiveness of these experimental subjects the interest of investigators in this field of chemistry is mainly due to the potential applications of dendrimers, for example, in industry as novel catalysts and materials for molecular electronic devices and light energy conversion, in medicine and in other fields.

In contrast with polymers formed by spontaneous polymerisation, dendrimers, which are oligomeric compounds (in principle, they can be polymeric), are prepared by multistep synthesis. There are two different methodologies, *viz*., the divergent and convergent approaches. In the divergent approach, dendrimers are constructed by the attachment of various fragments to a dendritic backbone (core). In this case, the molecule is built up layer-by-layer in the direction from the centre of the dendritic molecule to its periphery. The convergent methodology involves initial synthesis of dendrons, *i.e*., the branches of a dendrimer, which are then coupled to the dendrimer core. This process resembles the assembly of individual sections on a common base.

More complex dendritic molecules built out of individual fragments are constructed using methods of organic, organometallic or coordination chemistry employed for the preparation of supramolecular structures.

I P Beletskaya, A V Chuchurjukin Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax (7-095) 932 88 46. Tel. (7-095) 939 36 18. E-mail: beletska@org.chem.msu.su (I P Beletskaya), Tel. (7-095) 939 11 39 (A V Chuchurjukin)

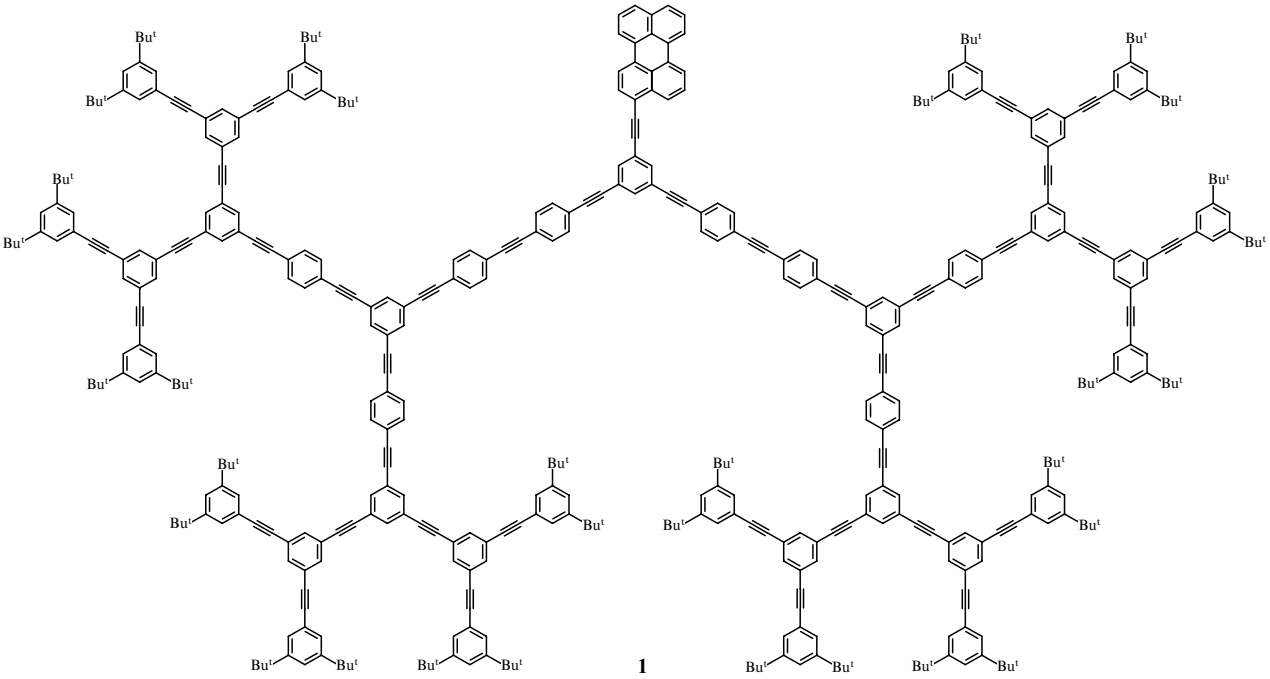
Received 23 February 2000
Uspekhi Khimii **69** (8) 699 – 720 (2000); translated by R L Birnova

Dendrimers have been described in numerous reviews;[1 – 12] however, the number of new types of dendritic molecules continues to increase. In writing this review, we were guided by our own interests and thus confined ourselves to the consideration of those dendrimers which incorporate ethynyl and aromatic fragments synthesised in reactions catalysed by transition metal complexes and dendrimers containing transition metal complexes as their cores or at the periphery where the metal is linked to the ligand by a coordination bond or by a carbon – metal bond. In many cases, we followed the path of the authors of the original publications who have discussed zero-generation molecules as matrices for future dendritic systems of the first, second and higher generations. It should be noted that our subdivision into sections is arbitrary, since many dendrimers comprise both arylethynyl fragments (which is the object of our particular interest) and transition metal atoms, leaving silicon-containing and many other dendrimers beyond the scope of consideration. In our attempt at a maximally complete coverage of the available material, we kept on adding novel data, but soon realised that we had to stop, otherwise this review would have never been written, for the number of publications is increasing every day.

II. Hydrocarbon dendrimers containing conjugated π-systems

Cross-coupling reactions catalysed by palladium complexes are widely employed in the synthesis of dendrimers containing ethynyl or *p*-phenylene fragments. This type of dendrimer presents substantial practical interest because it ensures structural rigidity and conjugation between the fragments, which are essential for directed energy and electron transfer and for the preparation of photoreactive materials.[13, 14] 1,3,5-Triethynylbenzene, which does not ensure conjugation between the substituents [15] on the periphery, can nevertheless transfer photoexcitation energy [13, 14] and represents a convenient core for the construction of such dendrimers. The photoreactive dendrimer **1**, the dendritic branches in which are linked together through ethynyl and *p*-phenylene bridges with a common focal point † of the dendrimer,[16] *viz*., the

† By the term 'focal point', the terminal point of the photoexcitation energy transfer in the molecule is understood in this case.

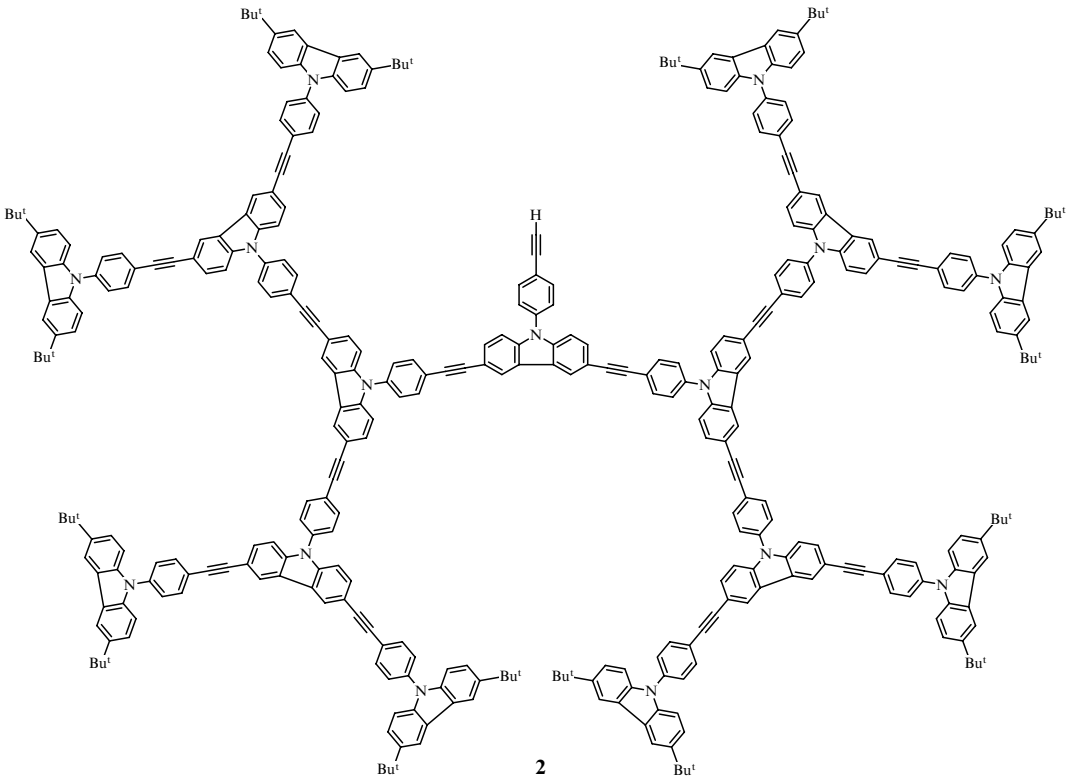


1

perylene fragment, may serve as an example. This dendrimer was synthesised by cross-coupling of a terminal acetylene with tribromobenzene according to the Sonogashira reaction.[17] Studies of the photophysical properties of this dendrimer revealed that on irradiation with light with the wavelengths corresponding to the absorption maxima of peripheral triethynylbenzene groups, the radiation intensity of the perylene fragment in the dendrimer exceeds that of free ethynylperylene by more than two orders of magnitude under identical conditions. In this case, the efficiency of the energy transfer from the periphery to the focal point of the dendrimer reaches 98%.[16]

Further investigations showed that the dendrimer of the next generation absorbs more light, but the efficiency of energy transfer to the focal point decreases.[18]

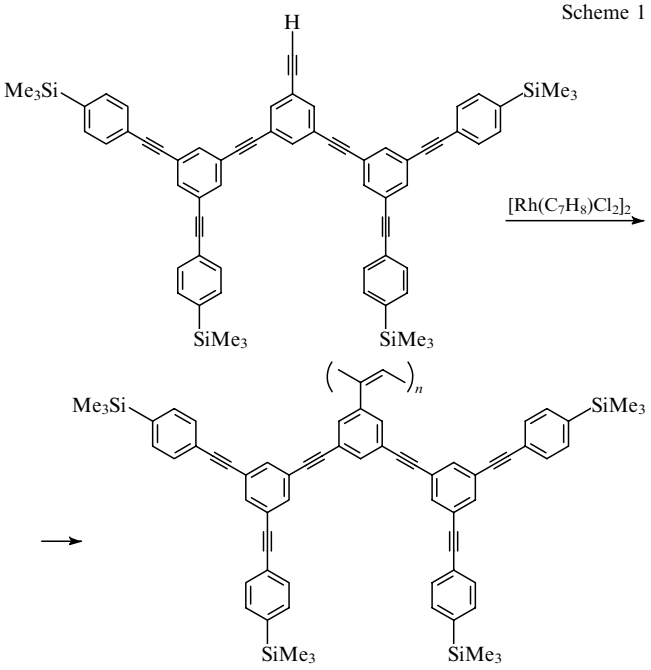
The dendrimers **2** containing 9-phenylcarbazole fragments linked through ethynyl bridges have been synthesised.[19] Such dendrimers are designed for the preparation of organic photoconductors (*i.e.*, compounds with non-linear optical properties), photo- and electroluminescent materials.



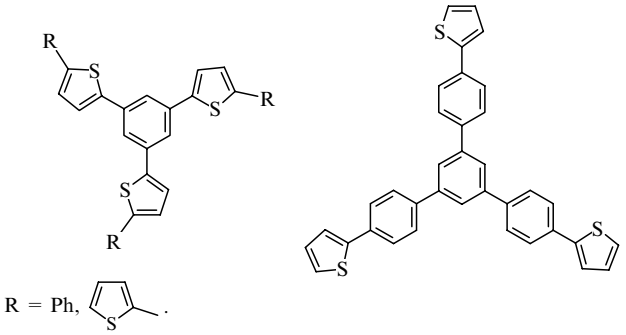
2

A dendrimer containing 1,3,5-triethynylbenzene fragments was used as the monomer unit in the synthesis of a polyacetylenic polymer (Scheme 1).[20]

Scheme 1



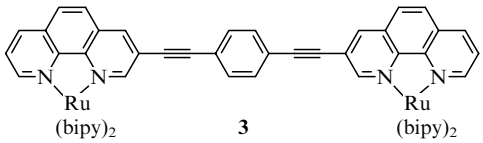
A series of zero-generation dendrimers containing thiophene groups were prepared by trimerisation of acetylthiophene derivatives in the presence of $SiCl_4$.[21]



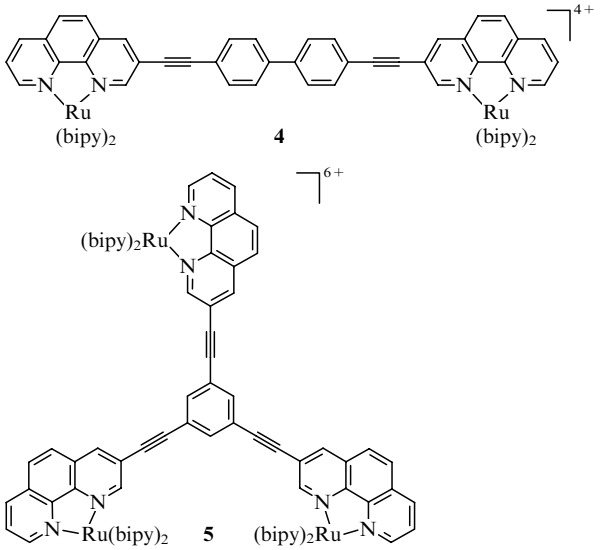
These compounds can be used in the synthesis of dendrimers, organic polymers of higher generations, semiconductors and liquid-crystalline materials.

III. Conjugated dendrimers containing transition metal atoms

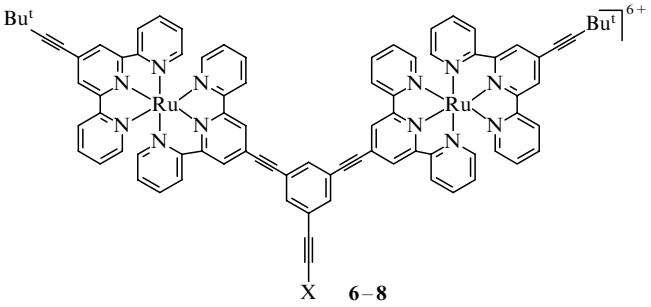
Conjugated systems, which contain several polydentate ligands coordinated to metal atoms within a single molecule, present substantial interest. Examples are provided by bi- (**3**, **4**) and trinuclear (**5**) complexes of ruthenium with a phenanthroline ligand synthesised by cross-coupling of a Ru–3-bromo-1,10-phenanthroline complex with 1,4-diethynylbenzene, 4,4′-diethynyl-1,1′-biphenyl and 1,3,5-triethynylbenzene, respectively.[15]

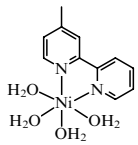


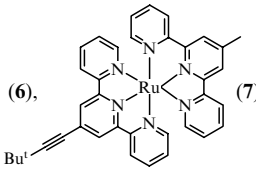
Measurements of the UV-spectra of the complexes thus prepared revealed that the main absorption bands of the bipyridine ligands do not change. Conjugation of the phenanthroline ligands in the binuclear complexes based on 1,4-diethynylbenzene (complex **3**) and 4,4′-diethynylbiphenyl (complex **4**) produced an additional low-energy absorption band. The absorption spectrum of the trinuclear complex **5** based on 1,3,5-triethynylbenzene more closely resembles that of the mononuclear complex, which points to the lack of conjugation between the substituents at positions 1, 3 and 5 of the central benzene ring.

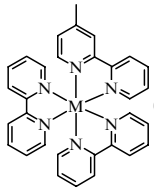


Luminescence studies of the heteronuclear complexes **6**–**8** containing both Ru and Ni, Ru and Cu or Ru and Os cations, which have been prepared by cross-coupling of Ru–phenanthroline complexes and the bipyridine complexes of Ni, Cu and Os with 1,3,5-triethynylbenzene, established that such complexes can transfer photoexcitation energy.[13]



X = 

(**6**), 

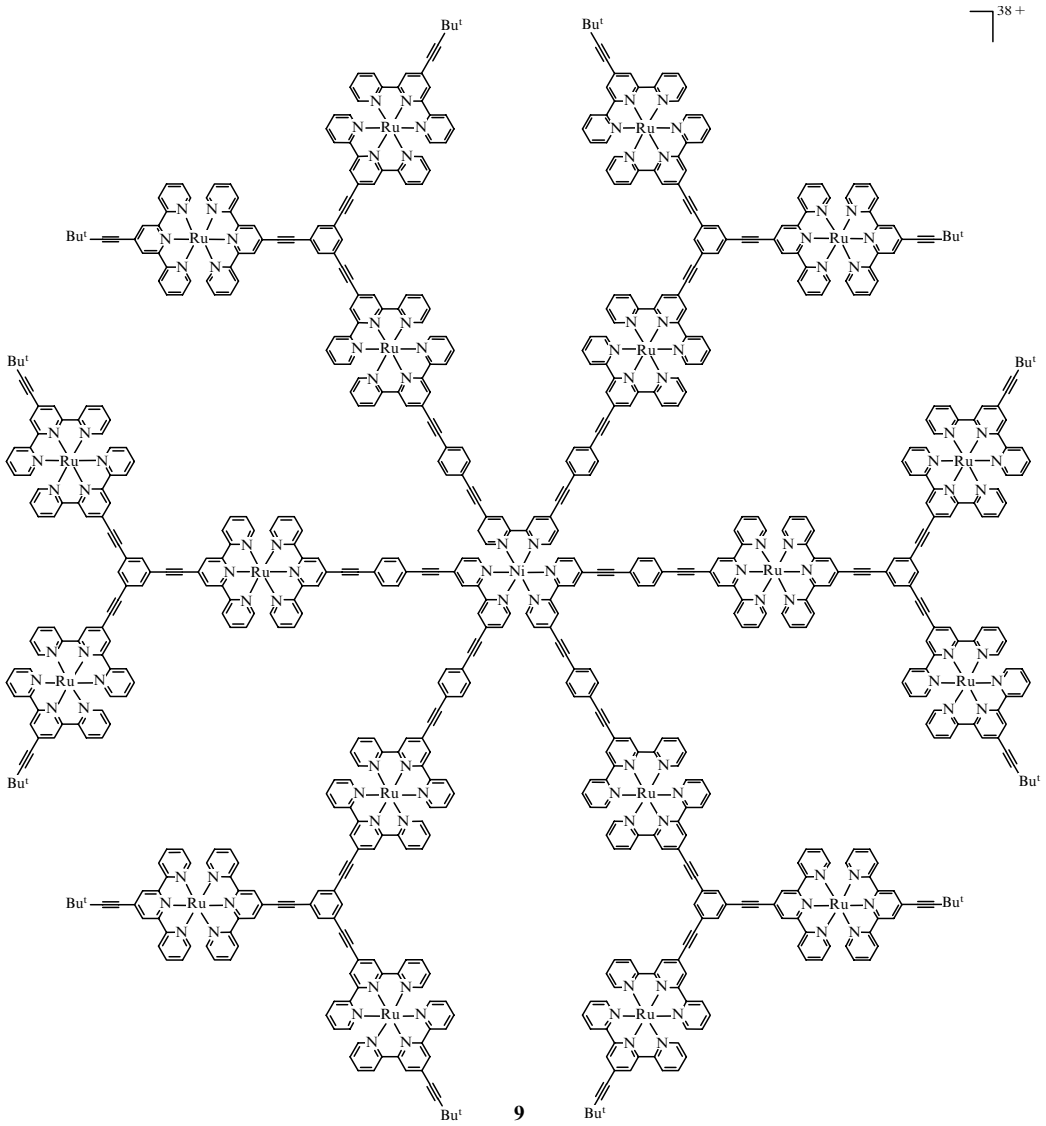
(**7**), 

(**8**)

M = Cu, Os.

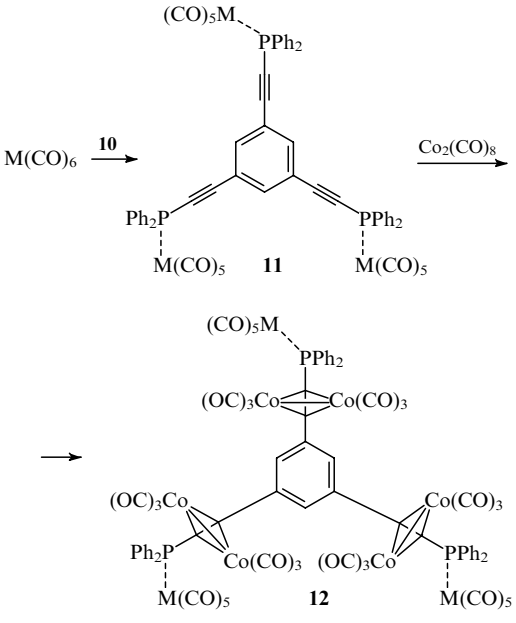
Thus the fragment **7** was used to build a more complex molecule **9**[14] in which the Ni–bipyridine complex is the central part of the molecular architecture. It is of note that the syntheses of complex molecules on the basis of fragments **6**–**8** have been accomplished with 67% to 78 % yields.

1,3,5-Triethynylbenzene was used as a basis for the synthesis of the tridentate phosphine ligand 1,3,5-$(Ph_2PC{\equiv}C)_3C_6H_3$ (**10**). To this end, 1,3,5-triethynylbenzene was metallated with 3 equiv. of n-butyllithium and the lithium derivative formed was introduced into the reaction with chlorodiphenylphosphine.[22] The

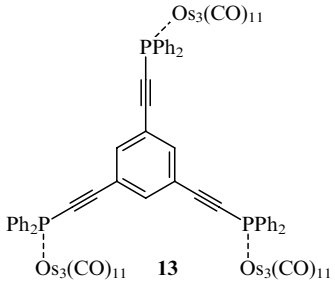


9

phosphine ligand **10** was first introduced into the reaction with the molybdenum or tungsten carbonyls $M(CO)_6$ (M = Mo, W) and the complexes **11** formed were treated with cobalt carbonyl $Co_2(CO)_8$. These reactions afforded compound **12**.

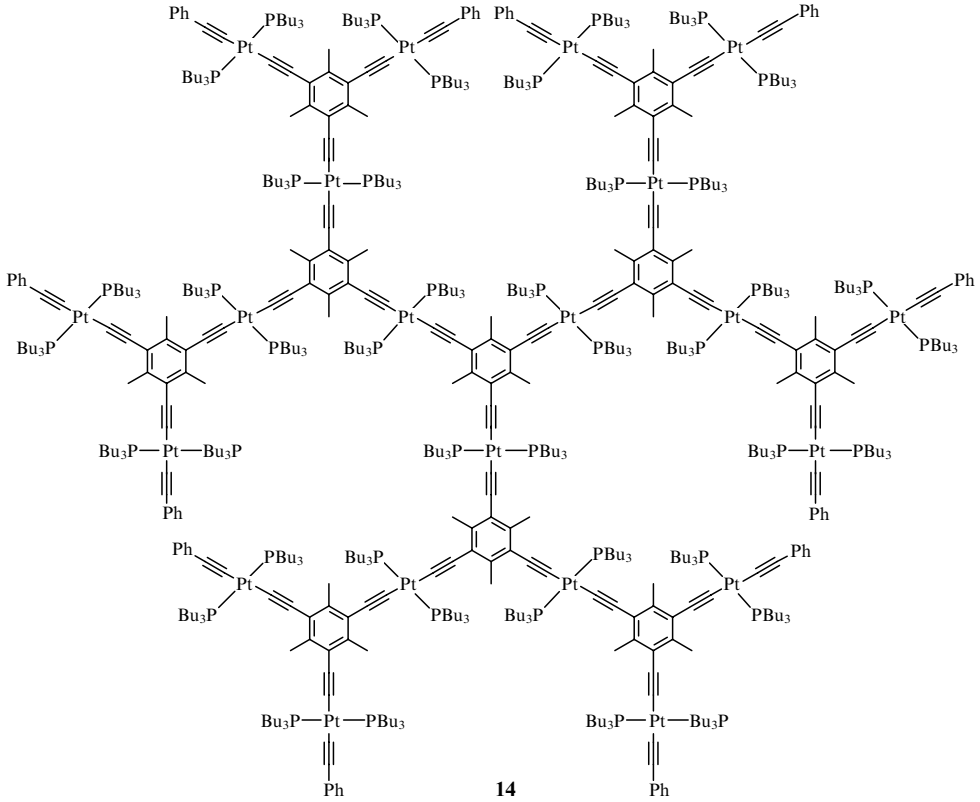


The osmium complex **13** was obtained in a similar way. In the latter case, the phosphine ligand **10** was coordinated to three $Os_3(CO)_{11}$ clusters.



True organometallic compounds constitute an additional type of dendritic conjugated systems. The platinum complex **14** with triethynylmesitylene ligands prepared by cross-coupling of triiodomesitylene with trimethylsilylacetylene with subsequent desilylation is an example.[23]

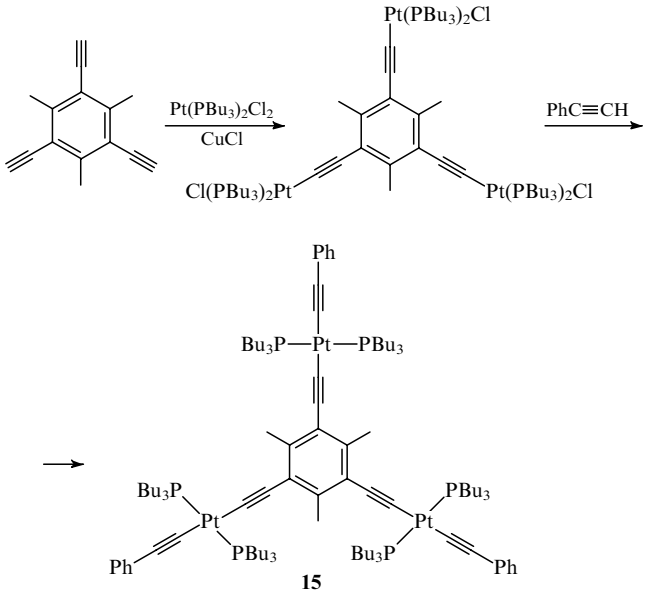
Triethynylmesitylene was introduced into the reaction with $Pt(Bu_3P)_2Cl_2$ in the presence of CuCl and further converted into the complex **15** by a reaction with phenylacetylene. Substitution of



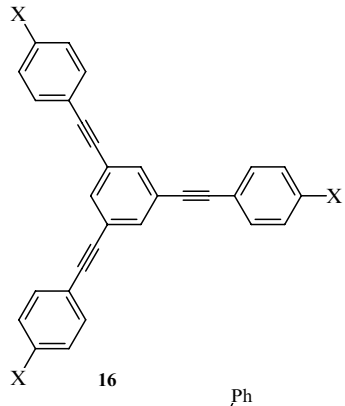
14

triethynylmesitylene for phenylacetylene yields first- and second-generation dendrimers.[23]

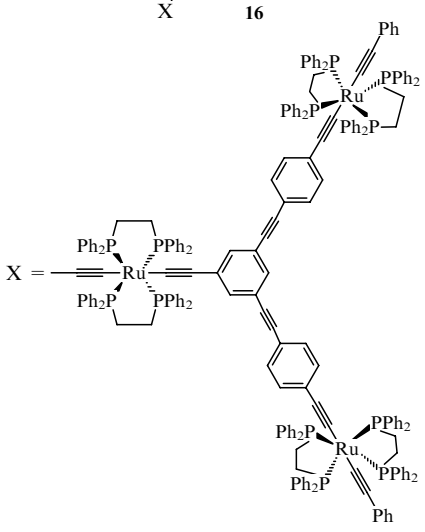
The organoruthenium dendrimer **16** was synthesised following the convergent approach.[24] It was shown that the introduction of ruthenium atoms into a conjugated π-system significantly enhances both the non-linear optical properties of the original compound and the two-photon absorption. These characteristics are also enhanced with the growth of the dendrimer.



15

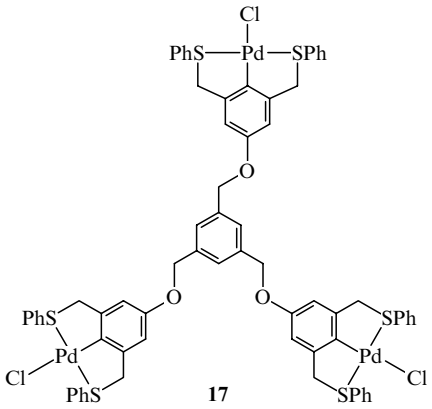


16



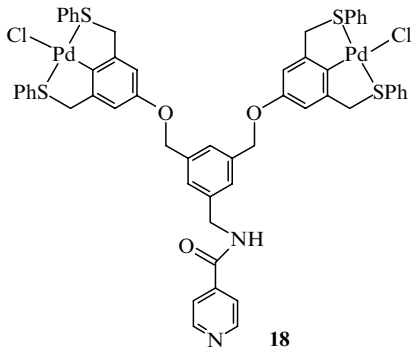
IV. Dendrimers containing pincer-type ligands and their metal complexes

The presence of pincer-type ligands at the periphery of zero-generation dendrimers facilitates their metallation with the formation of metallacycles. Thus the complexes **17** – **19** containing pincer-type SCS ligands were used as building blocks in the synthesis of more complex dendrimers.[25, 26] For example, the pyridine group in compound **18** or the cyano group in compound

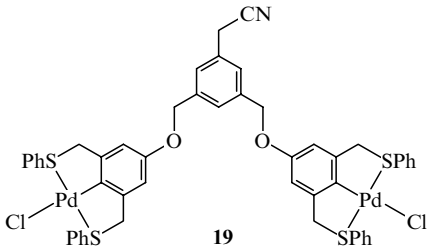


17

19 is coordinated to palladium atoms to yield cationic complexes. The dendrimer **20** synthesised on the basis of the complexes **17** and **18** represents an organometallic compound the dendritic structure of which is formed by coordination bonds. It is noteworthy that in this case the pincer group is incorporated into the dendrimer structure as the connecting link.

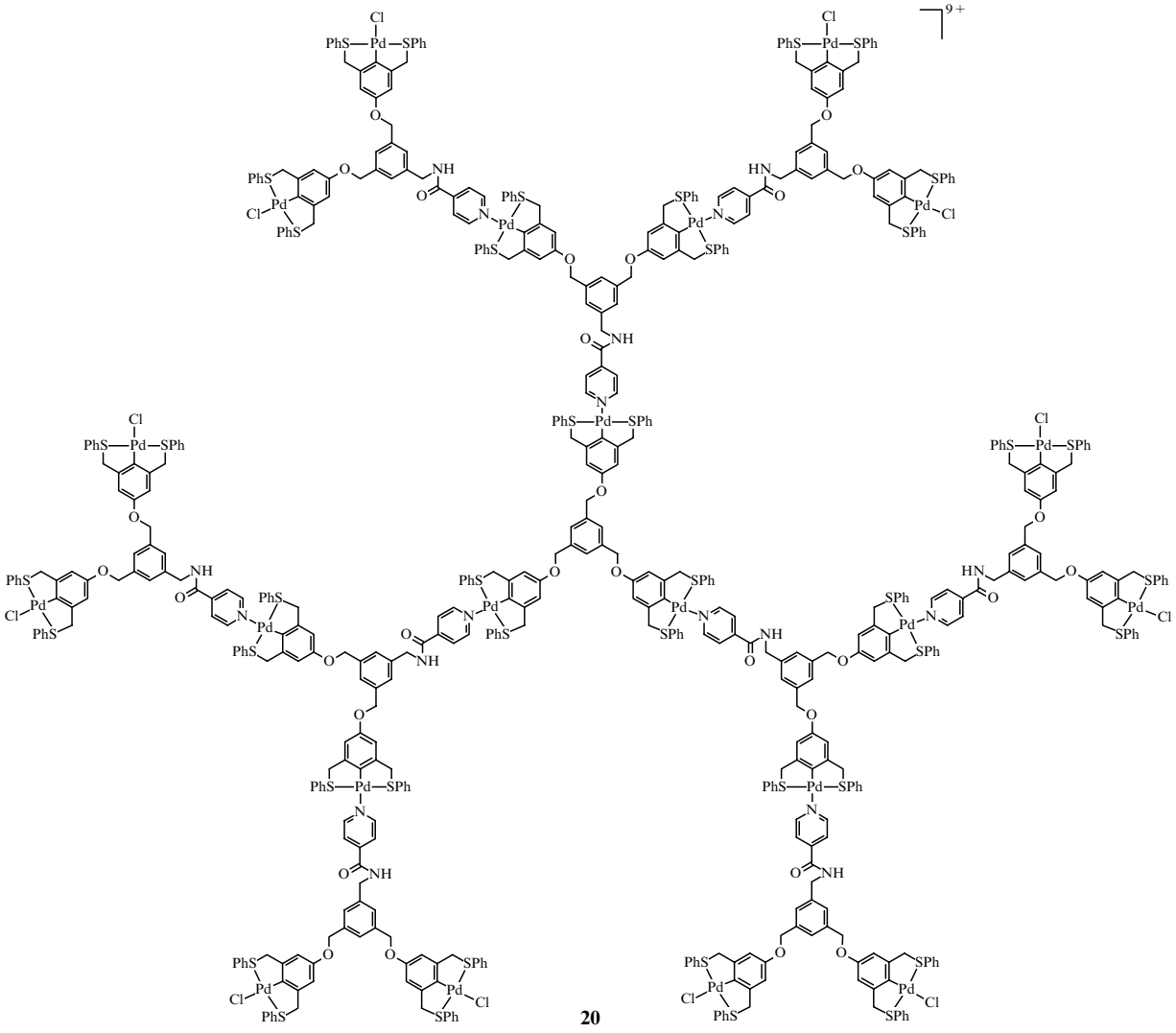


18



19

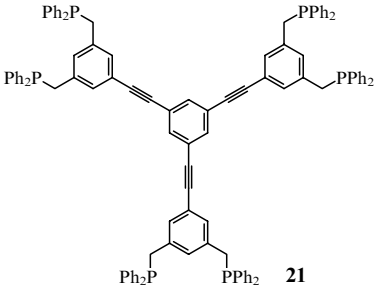
The presence of SCS pincer-type ligands strongly restricts the application of non-palladium transition metal complexes, since only cyclopalladation is possible. Replacement of SCS by PCP



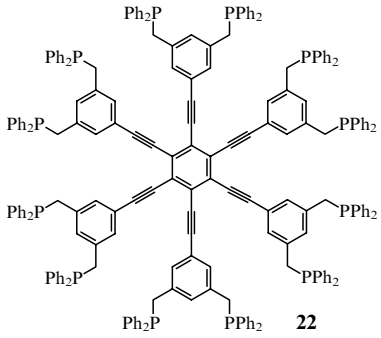
20

ligands made it possible to conduct cyclometallation with both Pd complexes and a variety of other transition metal compounds.

We made an attempt to synthesise zero-generation dendrimers on the basis of triethynyl- (**21**) and hexaethynylbenzene (**22**).[27, 28]

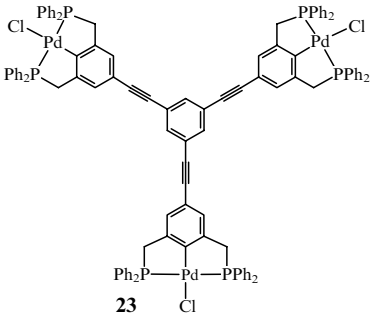


21

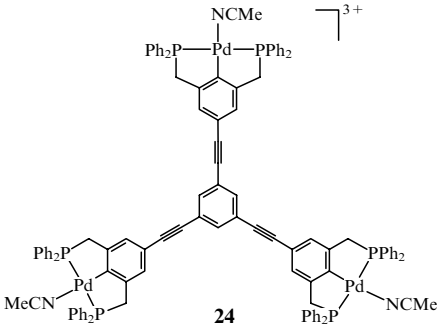


22

Cyclopalladation of triethynylbenzene **21** was successful. The corresponding trinuclear palladium complex **23** was obtained in 90% yield. However, cyclopalladation of the ligand **22** designed for the synthesis of a hexanuclear complex failed, since this reaction gave a mixture of compounds. We attribute this failure to the high degree of conjugation within the molecule, which prevents the introduction of six electron-withdrawing substituents. Yet another trinuclear palladium complex **24** prepared by cyclopalladation of the ligand **21** is an efficient catalyst for the Heck reaction.[29]

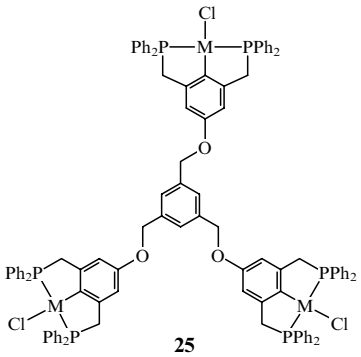


23

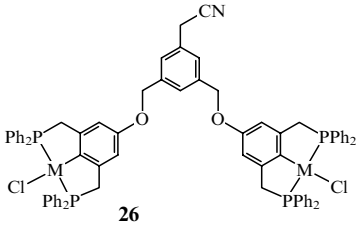


24

The applications of other transition metal complexes, *e.g.*, the Ni and Pt complexes **25** and **26** containing PCP pincer-type ligands, have been described.[30]



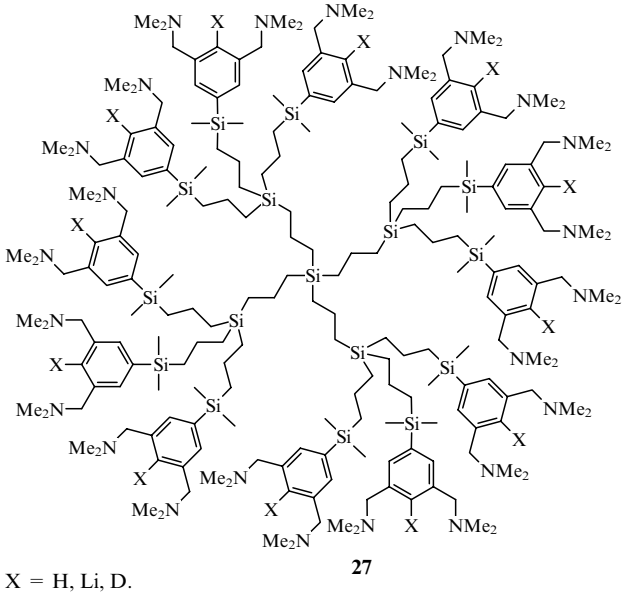
25



26

M = Ni, Pt.

A method for the introduction of the pincer-type NCN and CN ligands, *e.g.,* 1-[3,5-$(Me_2NCH_2)_2C_6H_3$] and 1-(4-Me_2N–$CH_2C_6H_4$) units, at the periphery of organosilicon dendrimers of zero (G_0) and first (G_1) generations has been proposed.[31] To this end, the corresponding bromo-substituted derivatives, *viz*., 1-Br-3,5-$(CH_2NMe_2)_2C_6H_3$ or 1-Br-4-$Me_2NCH_2C_6H_4$, were lithiated and introduced into the reaction with an organosilicon dendrimer containing the chlorosilane groups $Si(CH_2CH_2CH_2Cl)_3$ at the periphery. This approach was used in the synthesis of the organosilicon dendrimers $G_0-SiMe_2-C_6H_3(CH_2NMe_2)_2$-1,3, $G_0-SiMe_2-C_6H_4(CH_2NMe_2)$-4, $G_1-SiMe_2-C_6H_3(CH_2NMe_2)_2$-1,3 and $G_1-SiMe_2-C_6H_4(CH_2NMe_2)$-4. The dendrimers synthesised and model compounds were metallated with Bu^tLi and further deuterated. Compound $G_0-SiMe_2-C_6H_2(CH_2NMe_2)_2$-1,3-Li-2 (**27**, X = Li) was converted into a platinum derivative under the action of 12 equiv. of $PtCl_2(SEt_2)_2$.



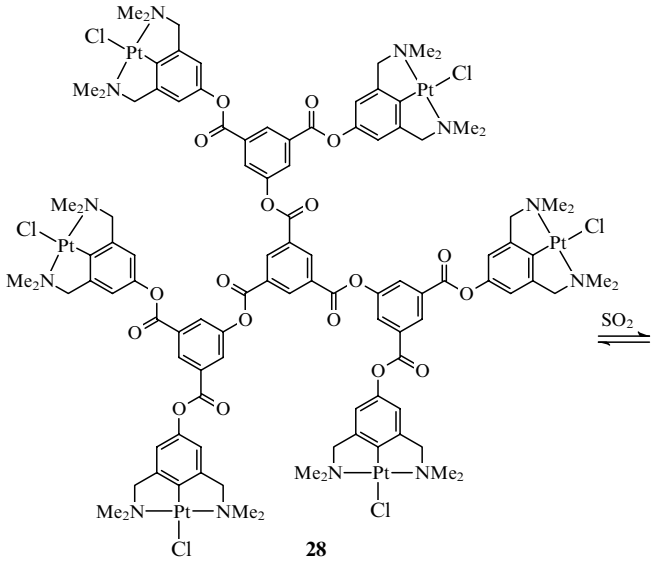
27

X = H, Li, D.

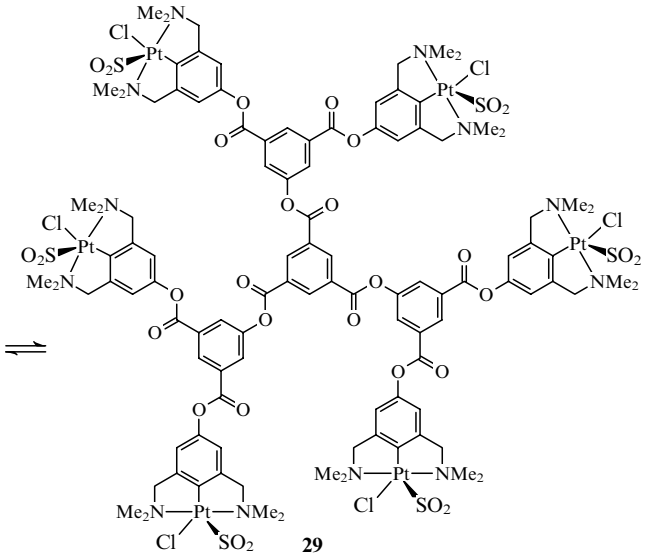
Catalytic activities of nickel complexes prepared on the basis of organosilicon dendrimers containing peripheral NCN pincer-type ligands were studied in the Kharash-type addition of CCl_4 to alkenes.[32] The kinetic data suggest that the catalytic activities of

zero- and first-generation dendrimers are lower than that of the monomeric catalyst (by 20% and 30%, respectively). However, complete separation of the catalyst from the reaction product by filtration through a membrane is an obvious advantage of dendrimers.[32]

The dendrimer **28** containing cycloplatinated fragments with pincer groups was used as a sensor in the determination of SO_2.[33,34] According to calculations, the molecule **28** is planar. In contrast with organosilicon dendrimers, this compound is poorly soluble in common organic solvents, which can be attributed to its structural peculiarities. Earlier studies have shown[33] that platinum and nickel complexes with NCN pincer ligands can reversibly bind SO_2; the resulting compound has the structure of a tetrahedral pyramid. The solubility of the complex formed is much higher than that of the starting compound. The dendrimer **28** (both in solution and in a solid state) reacts instantaneously with gaseous SO_2 to yield the corresponding addition products, which is accompanied by the appearance of an orange colour.



28



29

The formation of the adducts **29** was confirmed by ^{1}H NMR and UV spectroscopic data. The addition of SO_2 is reversible. The desorption of SO_2 occurs on heating of the adduct to 40 °C or *in vacuo*.

V. Dendrimers containing transition metal coordination complexes

1. Dendrimers containing coordination complexes with phosphine ligands

A search for novel catalytic systems stimulated the design of new ligands including those based on dendritic molecules with different electronic and spatial characteristics. It was anticipated that the use of dendritic ligands in combination with heterogenisation of a catalyst and biphasic systems would provide a clue to the problem of the catalyst's regeneration. Moreover, grafting of a catalyst on the surface of the dendrimer might enhance the regioselectivity by virtue of fixation of its conformation due to steric hindrances created by the dendrimer.[35] However, the experimental data available so far evidence that dendritic complexes manifest lower activities than their mononuclear analogues.[35] The reason for this may be related to steric hindrances and other problems due to larger sizes of dendrimers. Besides, the activity of a catalyst may be lost owing to the stabilisation of the complex by various functional groups present in the dendrimer.[35]

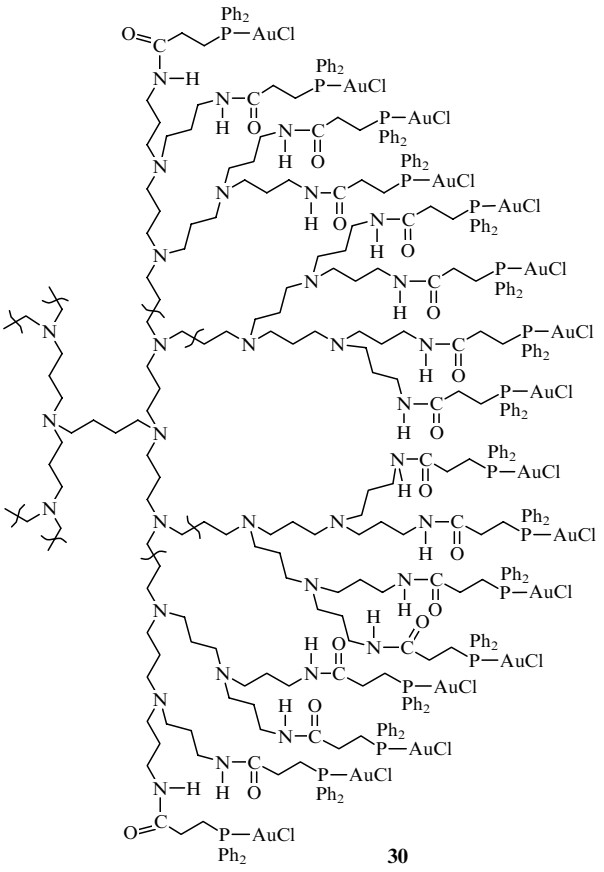
Tertiary phosphines can form complexes with virtually all transition metals; many of those efficiently catalyse various reactions. It is not surprising therefore that the overwhelming majority of publications are devoted to the dendrimers containing phosphine complexes of transition metals. Thus the synthesis of ruthenium complexes with phosphine-containing dendritic ligands was described and their catalytic activity was investigated.[35] However, reactivities of these dendritic complexes appeared to be lower than that of the original mononuclear complexes $RuH_2(PPh_3)_4$. Unlike the latter, dendrimers did not react with chloroform and formed insoluble compounds with alkenes which could not be characterised; these compounds slowly reacted with CO to give the corresponding carbonyls. Preliminary studies showed that dendritic ruthenium complexes displayed high catalytic activities in the hydrogenation of ketones.[35]

Synthesis of dendrimers containing bidentate phosphine ligands $[-CH=NN(CH_2PPh_2)_2]$ at the periphery and the preparation of platinum, palladium and rhodium complexes based on them have been described.[36] Dendritic platinum and palladium complexes were methylated in the reaction with MeMgBr and carbonylated by treatment with CO.

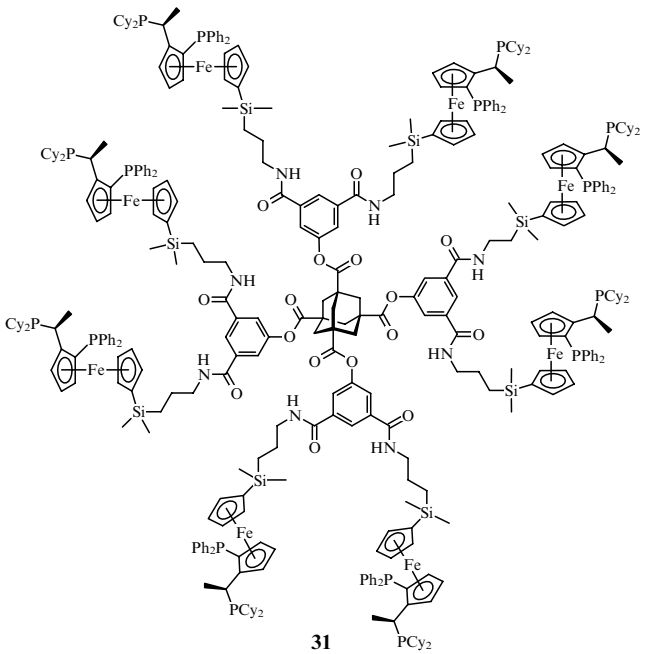
Dendritic polyamines containing terminal diphenylalkylphosphine groups, which are ideal ligands for the complexation with transition metals in lower oxidation states, have been synthesised.[37,38] The structure of one such compound (its right half is shown), *viz*., a multinuclear gold(I) complex with a fourth-generation dendrimer containing 32 terminal diphenylphosphine groups (complex **30**), is given below.[37]

X-Ray diffraction analysis of analogous gold(I) mono- and binuclear complexes revealed the presence of intermolecular NH···O hydrogen bonds in their crystal structures. It was suggested that similar intramolecular hydrogen bonds are also present in the Au complex with dendritic ligands. Such gold(I) multinuclear complexes represent a new class of metal-containing polymers with definite, probably spheric structures with dendritic molecules as the supporting matrices. These complexes can be used as catalysts and in medicine for biochemical diagnostics and as anti-inflammatory and anti-tumour drugs.[37]

Dendritic molecules containing chiral ferrocenyl phosphine ligands present special interest. Zero- (compound **31**) and first-generation dendrimers containing up to eight chiral diphosphine ligands were synthesised on the basis of benzene-1,3,5-tricarbonyl chloride and adamantane-1,3,5,7-tetracarbonyl chloride[39] and a silylated ferrocenyldiphosphine derivative $[C_5H_3(PPh_2)(CHMe.PCy_2)]Fe(C_5H_4SiMe_2CH_2CH_2CH_2Cl)$, where Cy is cyclohexyl.



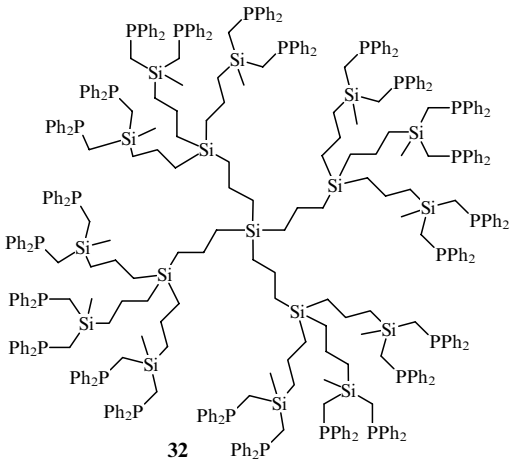
30



31

Catalytic properties of rhodium complexes prepared by the reaction of $[Rh(COD)_2]BF_4$ (COD is cycloocta-1,5-diene) with these dendritic ligands were studied in asymmetric hydrogenation of dimethyl itaconate. An enantiomer of dimethyl 2-methylbutane-1,4-diolate was obtained with *ee* 98%, which is only 1% lower than that achieved with a mononuclear complex.‡ This result is remarkable in that in this case the catalyst can be fully separated from the reaction products using membrane technology.

Dendrimers of the type **32** with peripheral diphenylphosphinomethyl ligands were synthesised from the organosilicon dendrimers $G_x-CH_2CH_2SiMeCl_2$ (x = 0, 1) by reacting them with $Ph_2PCH_2Li\cdot TMEDA$ (TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[41]



32

The reaction of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ with the dendrimer **32** afforded a palladium complex which was further used as a catalyst in the allylic alkylation of diethyl methylmalonate with sodium allyltrifluoroacetate in both a batch process and in continuous process using a membrane reactor. In the former case, the catalyst manifested an exceedingly high activity. The yield of the reaction product exceeded 80% after 30 min at a substrate : catalyst ratio of 2000 : 1 (see §). However, in a continuous membrane reactor at the same ratio of the reactants, the initially high catalytic activity was gradually almost extinguished following passage of 15 reactor volumes of the reaction mixture. The reaction mixture at the outlet from the reactor did not contain any catalyst. This loss of the catalytic activity was attributed to the decomposition of the palladium complex.

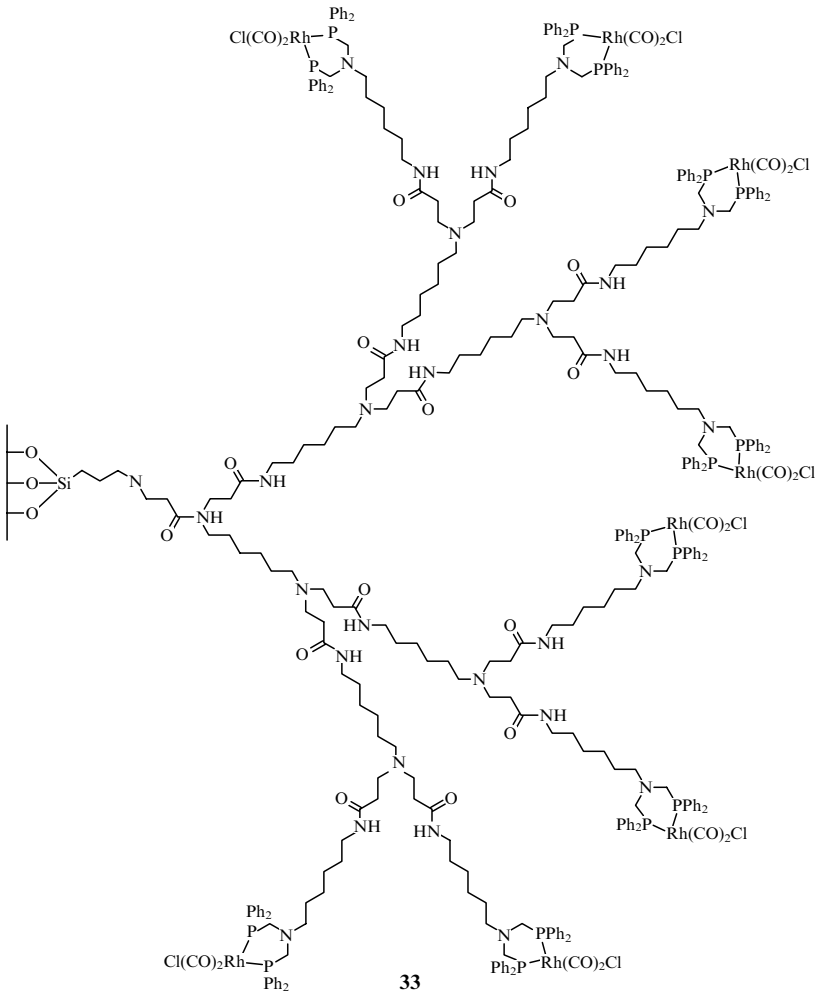
Synthesis of silica gel-grafted polyamidoamine dendrimers containing peripheral diphenylphosphinomethyl groups has been carried out.[42,43] These dendrimers were used to prepare the corresponding rhodium complexes **33** which present interest as recyclisable catalysts in the reaction of alkene hydroformylation and can be used, in particular, in the production of drugs of the ibuprofen and naproxen type.[42] Studies of the catalytic activities of such dendritic catalysts revealed that these activities increased with the increase in the length of the carbon chain between the amide and amine nitrogen atoms from two to six carbon atoms and did not change further. Such an increase in the catalytic activity seems to be due to the reduction of steric hindrances on the surface of the dendrimer.

Hydroformylation of styrene and vinyl acetate involving such catalysts occurred with virtually quantitative yields and high regioselectivity. The catalysts retained high catalytic activities over at least four cycles. However, slow wash-out ¶ of rhodium from the dendrimer immobilised on silica gel did occur.

‡ Mononuclear catalysts (ferrocene derivatives) are used in the commercial production of pesticides.[40]

§ With respect to 1 mol of the catalytically active groups.

¶ It is noteworthy that rhodium is not washed out from the catalyst with a pure solvent, but is washed out in the presence of CO or a $CO-H_2$ mixture, apparently, as a result of exchange of dendritic phosphine ligands in the rhodium complexes for CO.



33

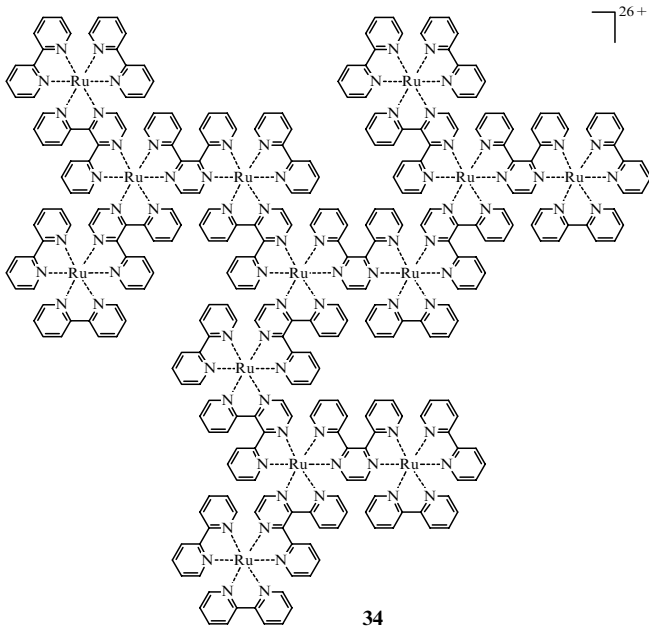
2. Dendrimers based on metal complexes with polypyridine ligands

In the foregoing section we considered the methodology of synthesis of metal-containing dendrimers based on the formation of new carbon–carbon or carbon-heteroatom bonds. Coordination of polydentate organic ligands around metal atoms is an alternative route to the construction of metal-containing dendrimers.[44] This procedure was used, in particular, in the synthesis of the dendrimer **34** containing ruthenium cations coordinated by 2,3-bis(2-pyridyl)pyrazine.[44]

In such dendrimers, transition metal coordination complexes function both as branching and linking blocks. These dendrimers are prepared using the 'complex-as-a-metal–complex-as-a-ligand' synthetic strategy in which a complex with free chelating groups ('complex-as-a-ligand') chelates a complex with labile ligands ('complex-as-a-metal'). This approach allows stepwise monitoring over the dendrimer growth and involvement of building blocks containing various metals or ligands at each stage of the synthesis.

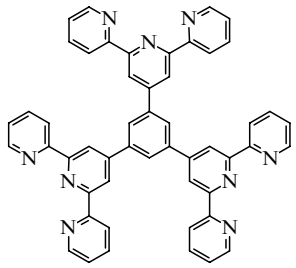
Dendrimers comprising complexes of different chemical nature can possess specific chemical properties, *e.g.*, provide gradients for electron transfer. Because of their remarkable photophysical and electrochemical properties, ruthenium(II) and osmium(II) complexes with polypyridine ligands represent ideal components for the synthesis of luminescent materials and other materials which can transform the light energy.[44]

Numerous dendritic compounds were synthesised based on 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) as the connecting ligands and 2,2′-bipyridine (bipy) as the terminal ligand.[44] These complexes contain several chromophore groups and a large number of redox centres.



34

2,2′ : 6′,2″-Terpyridine (terpy) and its derivatives were used as ligands in the synthesis of metal-containing fragments of dendrimers. The synthesis of 1,3,5-tris(2,2′ : 6′,2″-terpyridin-4′-yl)benzene,

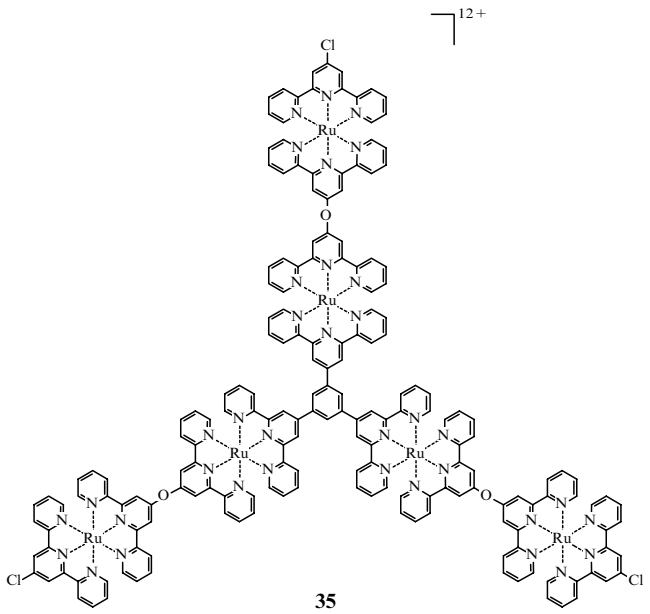


trinuclear[45] and hexanuclear (**35**)[46] ruthenium complexes prepared on its basis has been described.[45]

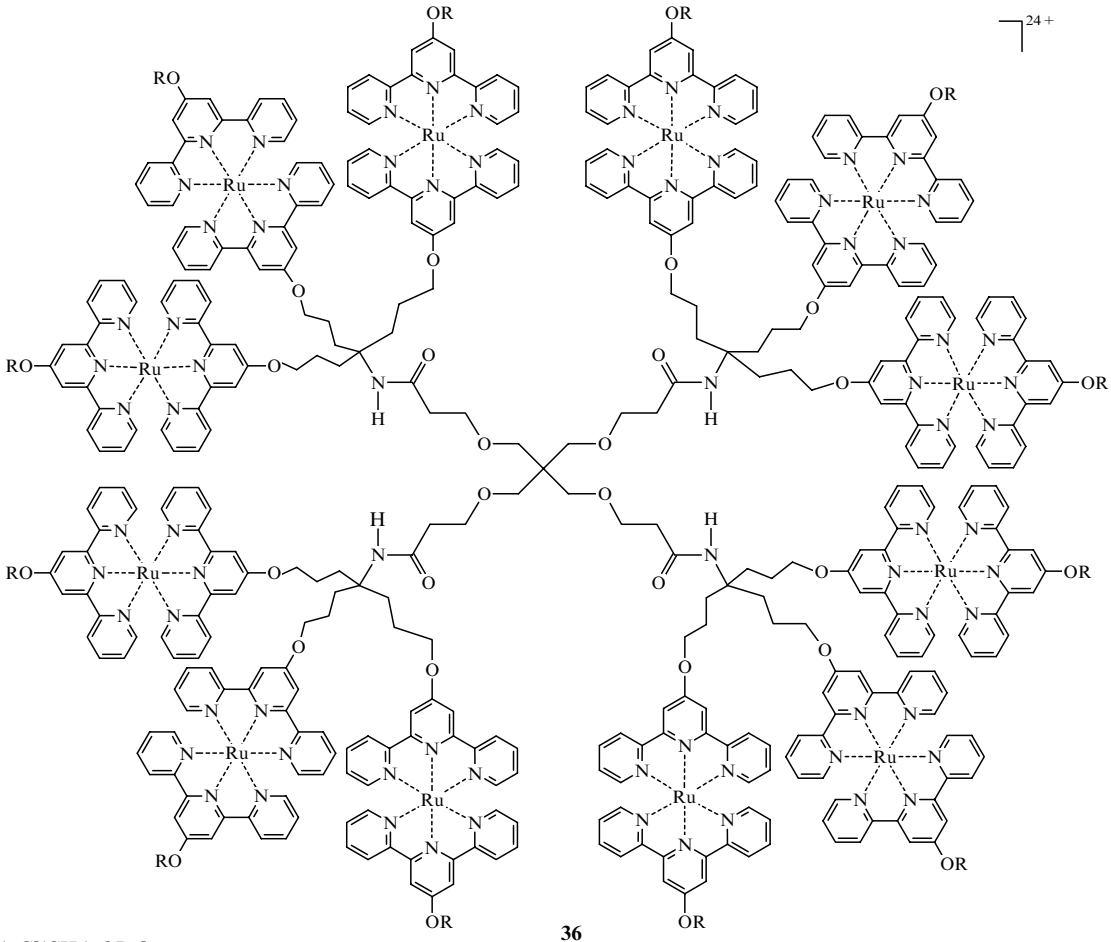
The dendritic complex **36** containing 12 ruthenium atoms was obtained by a reaction of 12 equiv. of (terpy)$RuCl_3$ with a polyamide-based dendritic ligand.[47]

The reaction of 1 equiv. of 1,3,5-tribromomethyl-2,4,6-trimethylbenzene with 3 equiv. of the ruthenium complex **37** was used to prepare the dendritic complex **38** containing six ruthenium atoms (Scheme 2).[48]

A similar reaction of 1 equiv. of hexabromomethylbenzene with 6 equiv. of compound **39** gave the dendritic complex **40** containing 18 ruthenium atoms (Scheme 3).[49] Studies of electrochemical properties of compound **40** revealed that all ruthenium centres are independent and do not apparently interact with one another.



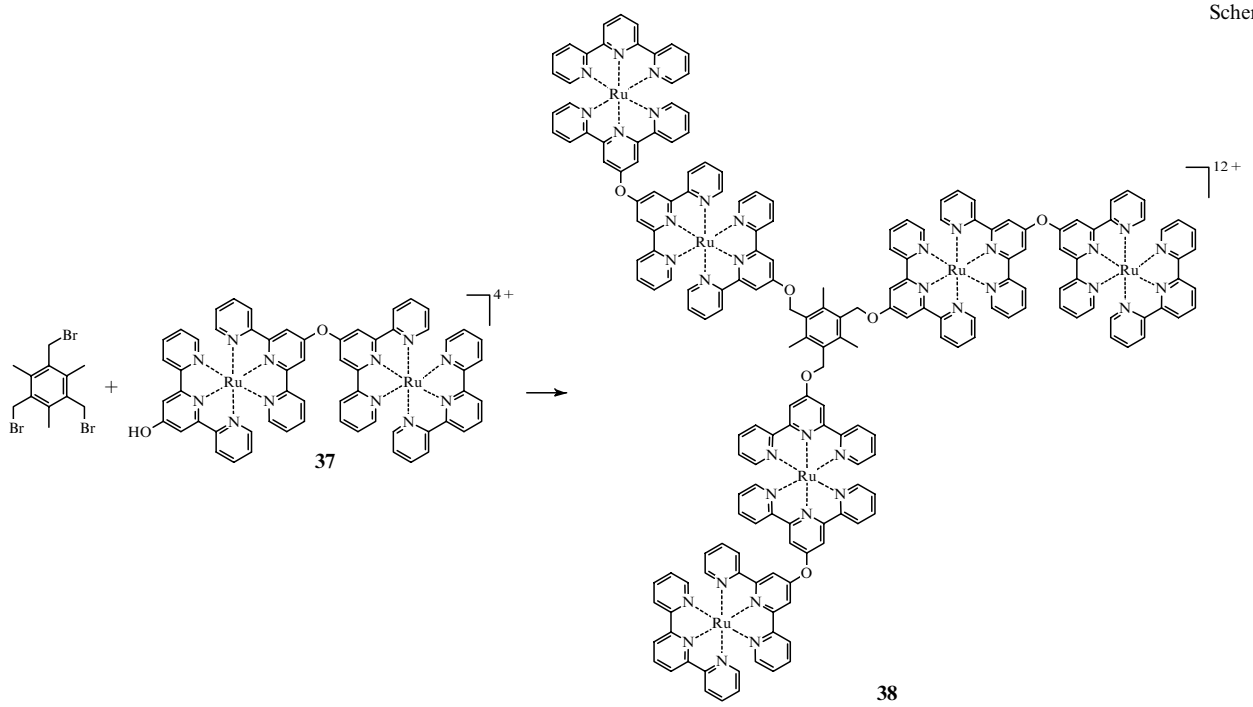
35



36

R = $(CH_2)_3C[(CH_2)_3OBn]$.

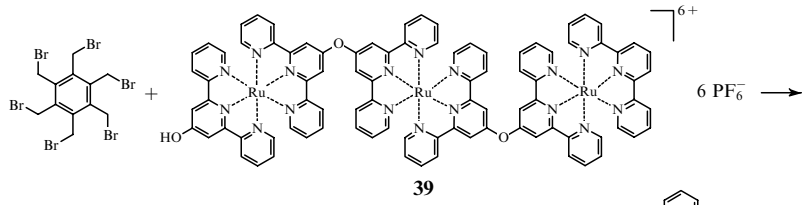
Scheme 2



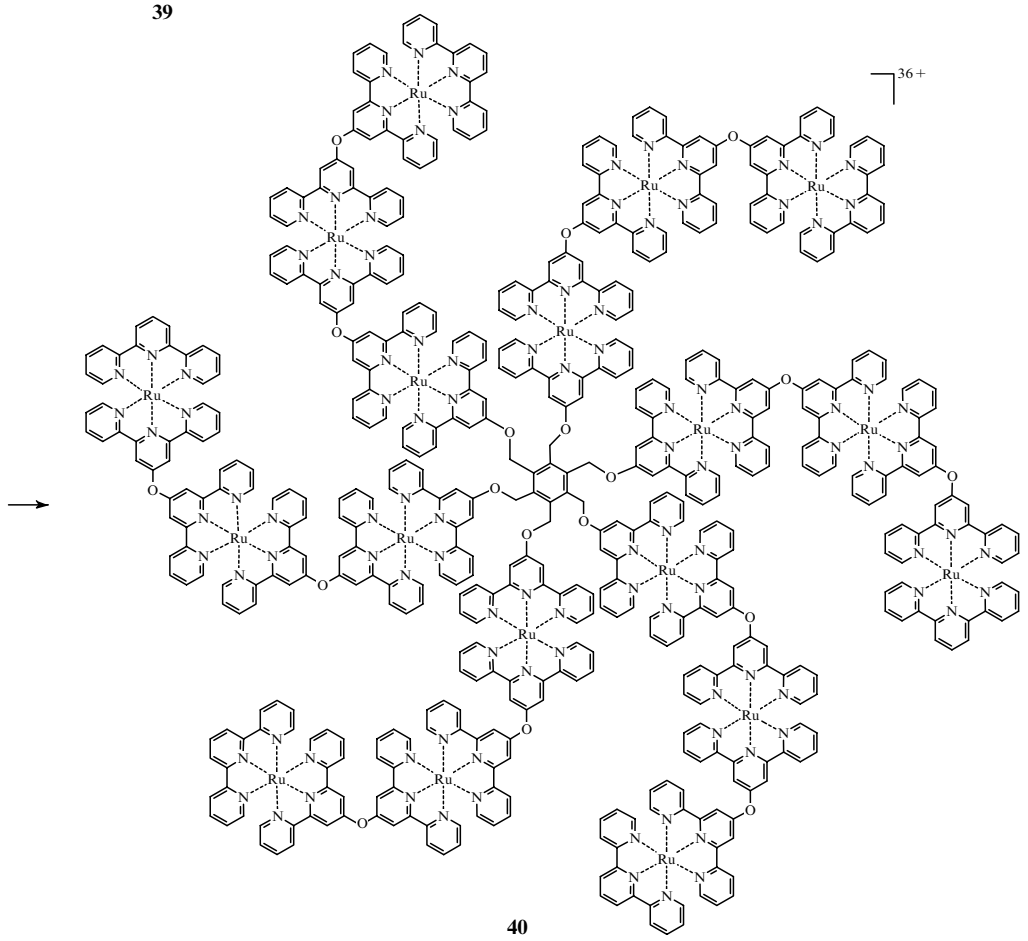
37

38

Scheme 3

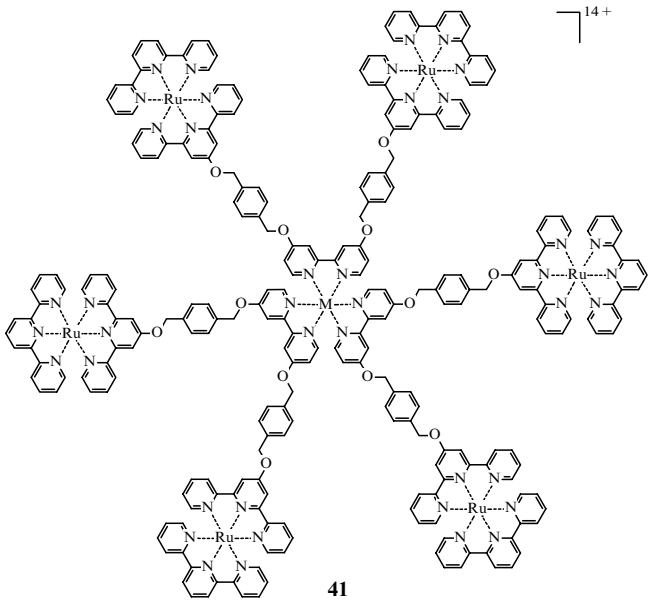


39



40

The dendrimers **41** containing ruthenium atoms at the periphery and iron or cobalt atoms in the core were prepared on the basis of polypyridine ligands.[50]

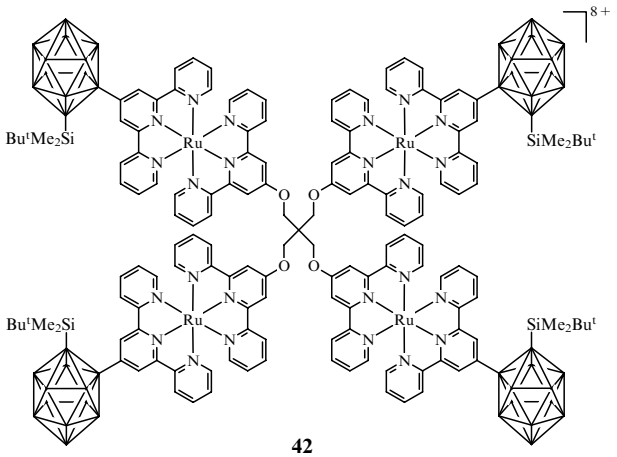


41

M = Fe, Co.

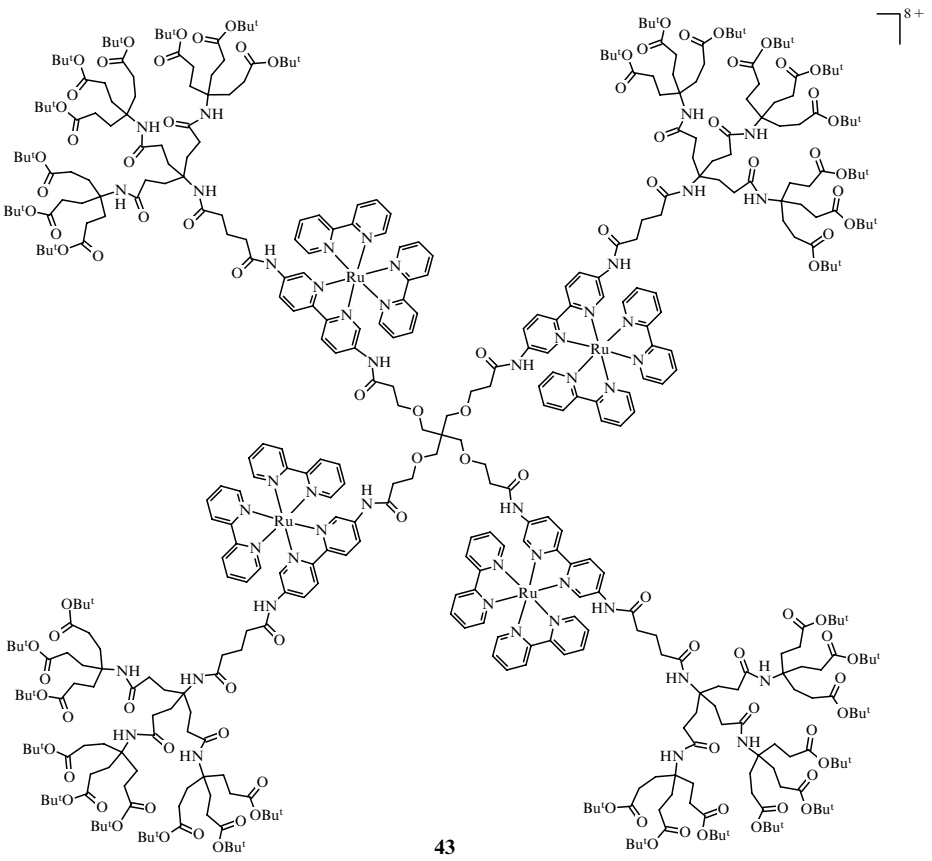
The central fragment of the dendrimer **41** was synthesised by complexation of a substituted bipyridine ligand to iron(II) or cobalt(II) ions.[50] The complex formed was introduced into reaction with a terpyridine ruthenium complex. Studies of electrochemical properties of the dendrimers revealed that a reversible redox process Ru(II) ⇌ Ru(III) can occur at +0.81 V; however, no apparent redox reaction involving iron or cobalt ions in the dendrimer core could be detected.[50]

The incorporation of four bulky carborane groups at the periphery of the pentaerythritol-based ruthenium-containing dendrimer (complex **42**)[51] resulted in restrictions of the conformational mobility, which was confirmed by magnetic non-equivalence of four methylene groups in the core and of two methyl groups at the periphery of the dendrimer. This had no effect on the electrochemical characteristics of the polypyridine ruthenium complexes of the type **42**.



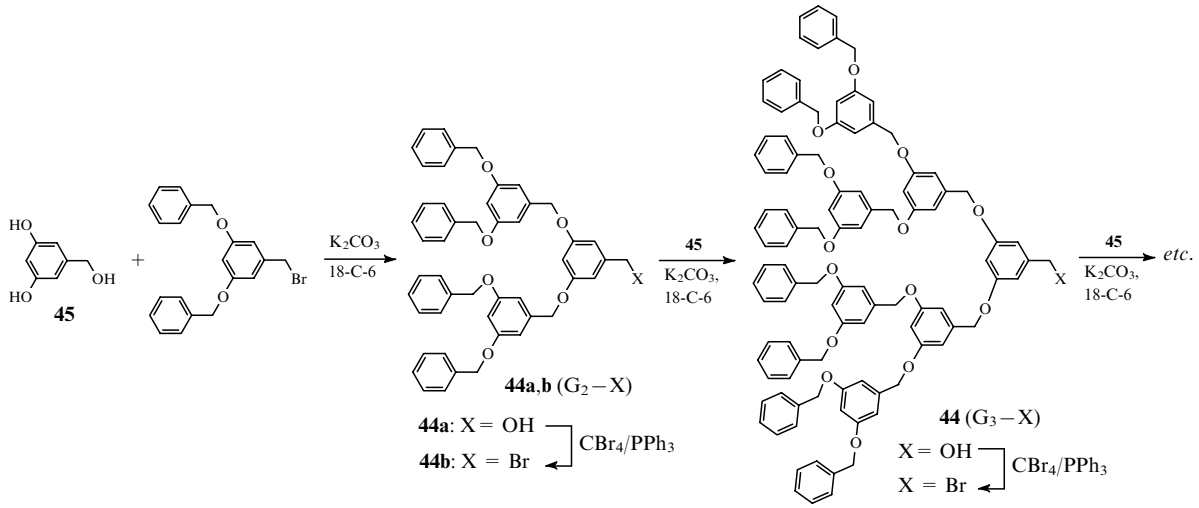
42

The dendrimer **43** containing four ruthenium complexes with bipyridine ligands has been described.[52] The NMR spectra of this dendrimer are extremely complex; therefore, its structure was established on the basis of UV spectroscopy, MALDI-TOF mass spectrometry and cyclic voltammetry.



43

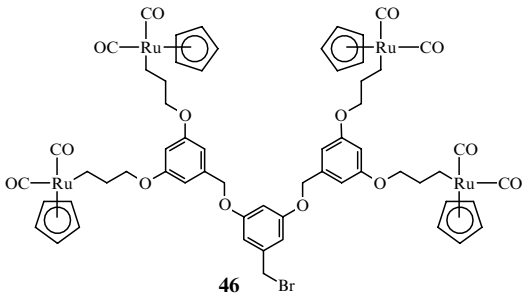
Scheme 4



VI. Dendrimers containing complexes with metal – carbon σ-bonds

The convergent approach was used [53] in the synthesis of the dendrimers **44** with 3,5-dibenzyloxybenzyl groups at the periphery (Scheme 4). 3,5-Dihydroxybenzyl alcohol (**45**) has been used as the monomer. It was noted [54] that the advantage of the convergent strategy is that it allows accurate monitoring of the number and localisation of functional groups in the final product. The intermediate products were isolated, purified and characterised after each step. Since all the intermediate and final products are easily soluble, the course of the reaction was monitored by NMR spectroscopy. Thus, any potential defects which might occur in the synthesis of dendrons could be detected prior to their attachment to the central fragment of the dendrimer.

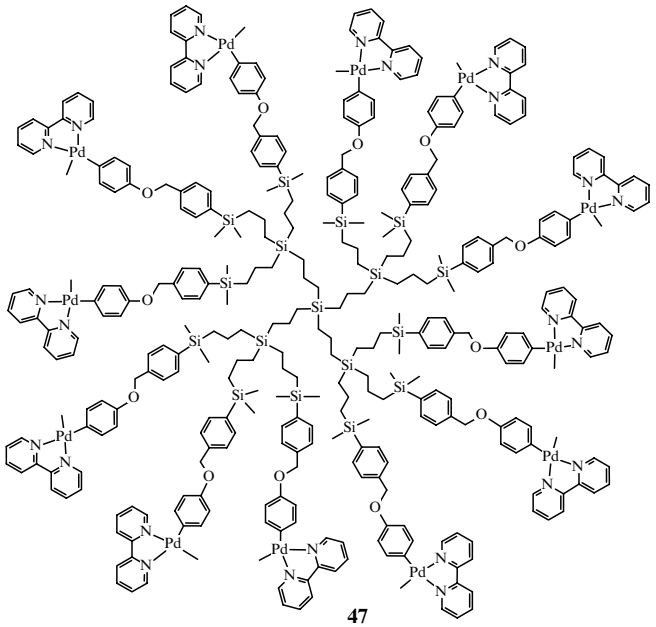
The organoruthenium compounds of the type **46** were synthesised in a similar fashion.[54] The resulting metal-containing dendrimers were rather stable, which made it possible to synthesise larger dendritic structures containing Ru – C π- and σ-bonds.



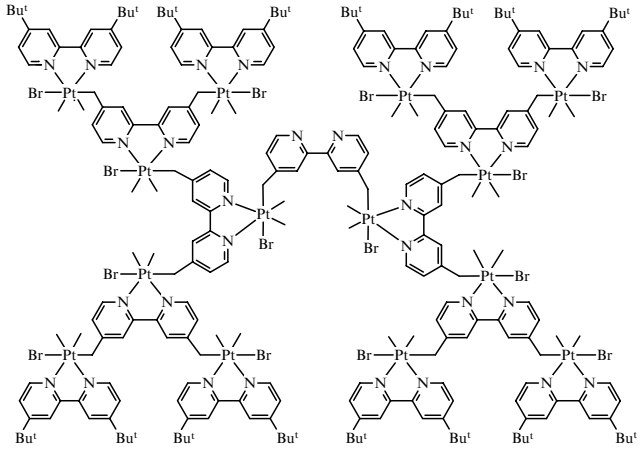
This approach was used in the synthesis of third- and fourth-generation dendrimers containing up to 48 ruthenium atoms.[54] All the organoruthenium compounds thus prepared are readily soluble in common organic solvents.

A first-generation organosilicon dendrimer containing 12 peripheral organopalladium units was synthesised by oxidative coupling of the $[Pd_2(dba)_3 \cdot dba/TMEDA]$ complex (dba is dibenzylidenacetone) to a dendrimer containing iodoarene groups. Further reaction of the metal-containing dendrimer with MeLi and bipyridine [55] resulted in the dendrimer **47**.

The oxidative addition of benzyl bromide to the Pd-containing dendrimer **47** was studied. The stability of the newly formed dendrimer containing organic derivatives of Pd(IV) and the main pathways of its decomposition were determined.



The synthesis of organoplatinum dendrimers of the type **48** has been described.[56] This involved the attachment of benzyl halides (RX) to $[PtMe_2(NN)]$ (where NN is the diimine ligand, *e.g.*, 2,2′-bipyridine). The reaction occurs with quantitative yields; however, the synthesis of larger dendrimers is complicated, since the solubility of the reaction products decreases as the size of the molecule increases. This reaction was followed by a colour change from orange-red (Pt^{II} complexes) to pale yellow (Pt^{IV} complexes). The increase in the chain length was repeated until NMR spectroscopy showed that the products contained structural defects. Larger organoplatinum dendrimers were obtained if the ligands were modified by introduction of *tert*-butyl groups, which increased the solubility of the dendrimers.[57] This synthesis employed a convergent strategy. The $[Pt_2^{IV}Me_4(\mu\text{-}SMe_2)_2]$ complex and 4,4′-bis(bromomethyl)-2,2′-bipyridine were used as the monomer units. The dendrimer **48** containing 14 platinum atoms was the last member of the series that has been synthesised. An attempt at preparing a dendrimer of the next generation containing 30 platinum atoms failed.

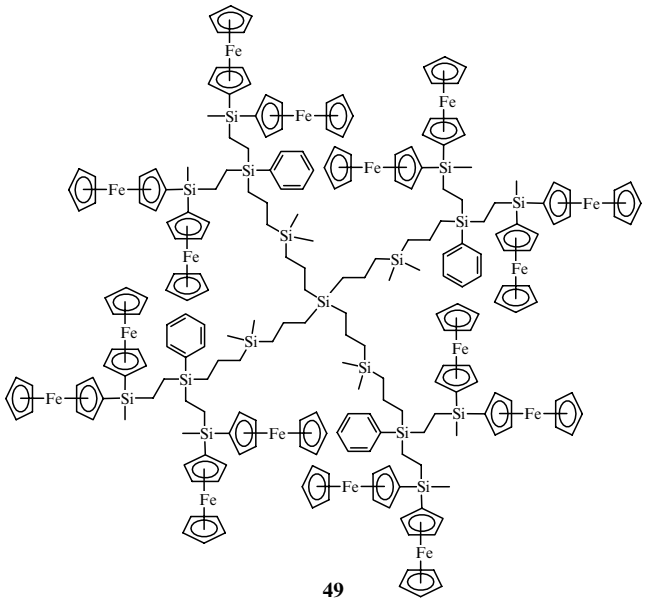


48

More recent studies [58] were aimed at investigating the possibility of synthesising multinuclear organopalladium compounds and bimetallic palladium–platinum dendrimers by the convergent approach. These studies showed that in this case the use of organopalladium compounds is limited because of the tendency of palladium(IV) complexes to undergo a reverse reaction, *viz*., to the reductive elimination of alkyl halide.

VII. Dendrimers containing terminal ferrocenyl groups

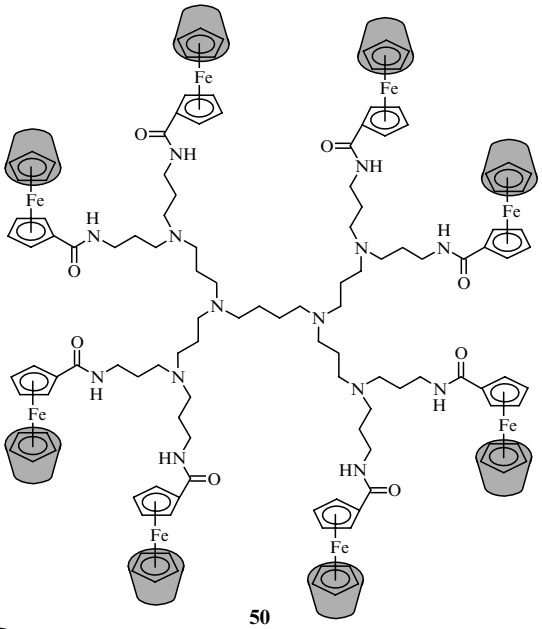
The majority of iron-containing dendrimers reported so far contain iron in the form of ferrocenyl groups. This can be explained by the fact that the chemistry of ferrocenes is well-studied and its derivatives are rather stable compounds. The synthesis of such systems aimed at the construction of dendrimers which could undergo redox reactions involving electron interactions between the metal-containing fragments.[59] The electronic interaction between the transition metal atoms within one of such dendrimers (**49**) has been studied; its structure is shown below.



49

Polymers containing ferrocene derivatives are currently used for modification of electrodes and redox catalysts and biosensors.[60] The cation $[FeCp(arene)]^+$ can be used as a starting material in the synthesis of dendrimers by the polyalkylation reaction. $[FeCp(C_6Me_6)]PF_6$ reacts with an excess of a base and ferrocenylalkyl halide $I(CH_2)_4Fc$ (Fc is $C_5H_5FeC_5H_4$) resulting in selective hexasubstitution to give $\{FeCp[C_6(CH_2)_5Fc]_6\}PF_6$. According to cyclic voltammetry data, all the six ferrocenyl groups are electrochemically equivalent, being oxidised at the same potential. The positive charge in the central fragment of the molecule has no effect on the oxidation process.[60]

The dendrimer containing peripheral ferrocenyl groups can form inclusion compounds with cyclodextrins (see, *e.g*., compound **50**) [61] localised at its periphery where they form a supramolecular structure of an even greater size.



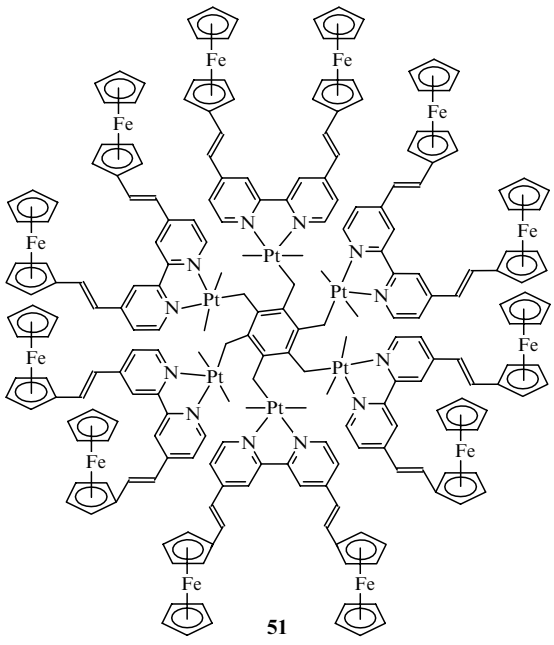
50



— β-cyclodextrin.

The number of ferrocenyl groups incorporated into cyclodextrin molecules is limited by steric hindrances on the surface of the dendrimer. In the case of the dendrimer **50,** the reaction between the ferrocenyl groups and cyclodextrin is complete.

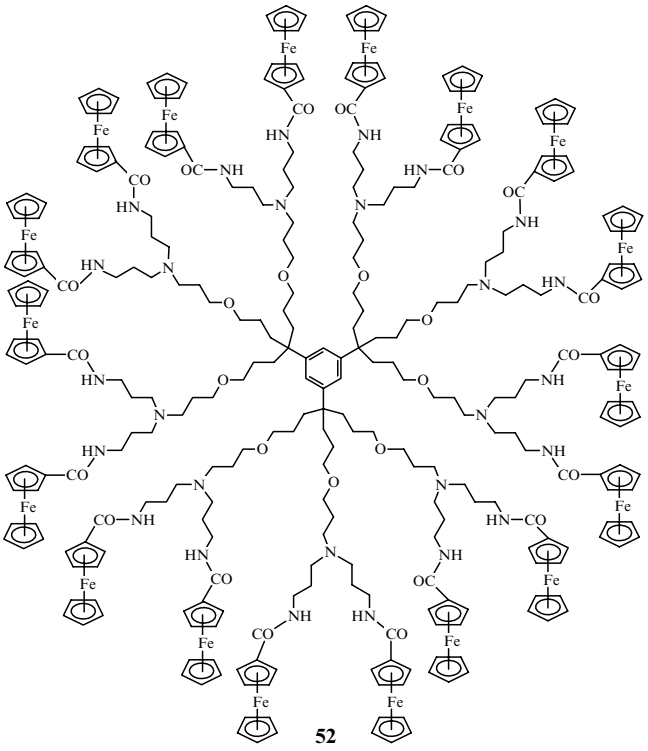
The synthesis of an unusual dendritic molecule **51,** which simultaneously incorporates Fe and Pt atoms (the platinum fragments in the centre and the ferrocenyl groups at the periphery), has been described.[62]



51

In this case, the dendritic molecule was assembled from fragments containing one platinum atom and two ferrocenyl units, which were attached to the central fragment, *viz*., hexakis(bromomethyl)benzene. This dendrimer was characterised by electrochemical and spectroscopic methods.

Dendrimers of the type **52** containing peripheral ferrocenyl groups linked to the central fragment through the amide groups have been used as sensors in the determination of inorganic anions (Cl^-, NO_3^- and HSO_4^-, see Ref. 63). Cyclic voltammograms of such dendrimers have the forms of simple reversible waves, which suggests that all of the ferrocenyl groups are equivalent in the oxidation process of Fe(II)/Fe(III).[63] In this case, the 'sensitivity' of the dendrimers to the nature of the anion in the redox process increases on going from zero- (G_0) to the first-generation dendrimers (G_1), reaching a maximum for a second-generation dendrimer (G_2) preceding the third-generation dendrimer (G_3) where steric saturation of the surface with the ferrocenyl groups takes place. With an increase in the generation number, the ferrocenyl groups on the surface of the dendrimer become more closely spaced; this results in a decrease in the sizes of the cavities where the anions could penetrate.

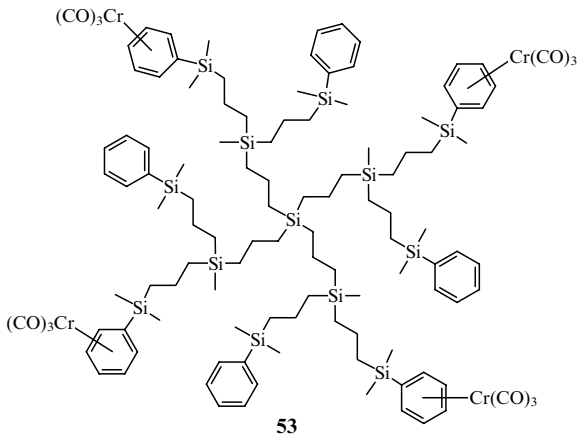


52

An optimal dendrimer for smaller anions is that belonging to a generation in which the number of ferrocenyl groups precedes steric saturation of the surface, which ensures the most suitable bulk of the cavities.[63]

VIII. Dendrimers containing transition metal π-complexes

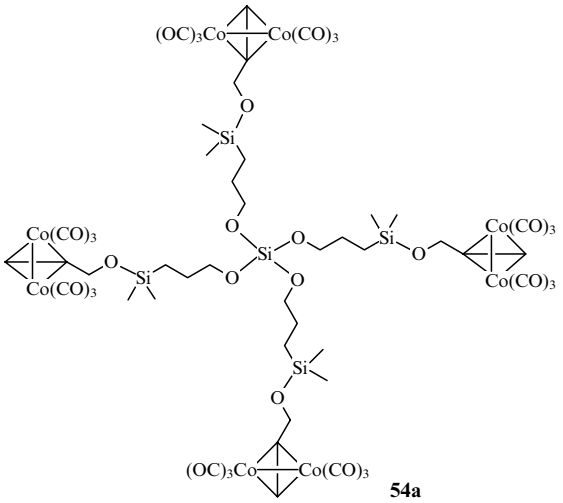
One of the ways of modification of dendrimers containing arene groups at the periphery consists in the formation of π-arene complexes of transition metals. Thus, the synthesis of first- and second-generation organosilicon dendrimers (*e.g*., the dendrimer **53**) containing aromatic rings with the $Cr(CO)_3$ groups linked has been described.[64]



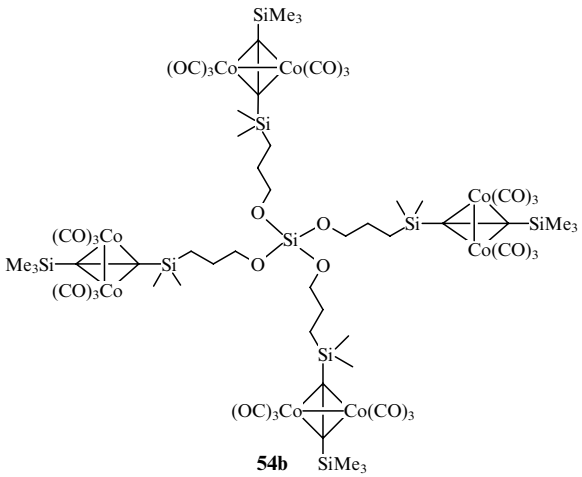
53

The starting organosilicon dendrimer was obtained by stepwise hydrosilylation and allylation. To this end, tetravinylsilane was introduced into the hydrosilylation reaction with methyldichlorosilane; the product formed was allylated with allylmagnesium bromide and repeatedly hydrosilylated with phenyldimethylsilane. The complexation involved only four out of eight benzene rings. The attempts to prepare a dendrimer with eight chromium atoms failed, since this required more drastic reaction conditions which resulted in the decomposition of the dendrimer.

Some first-generation organosilicon dendrimers containing peripheral alkyne groups further converted into the cluster π-complexes **54a** and **54b** by a reaction with $Co_2(CO)_8$ have recently been synthesised.[65]

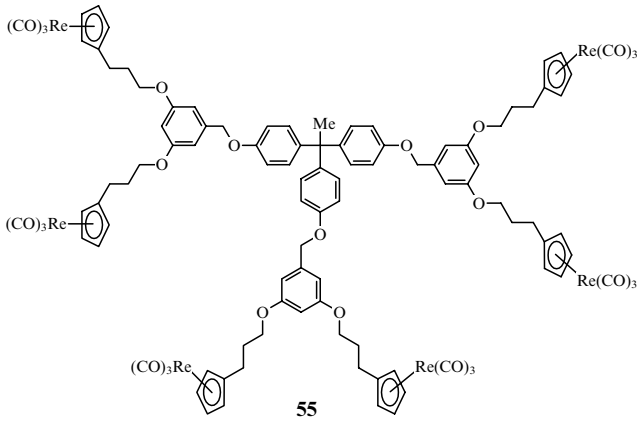


54a



54b

The organometallic dendrimer **55** containing six peripheral rhenium atoms was synthesised from the 3,5-dihydroxybenzyl alcohol using the convergent approach.[66]



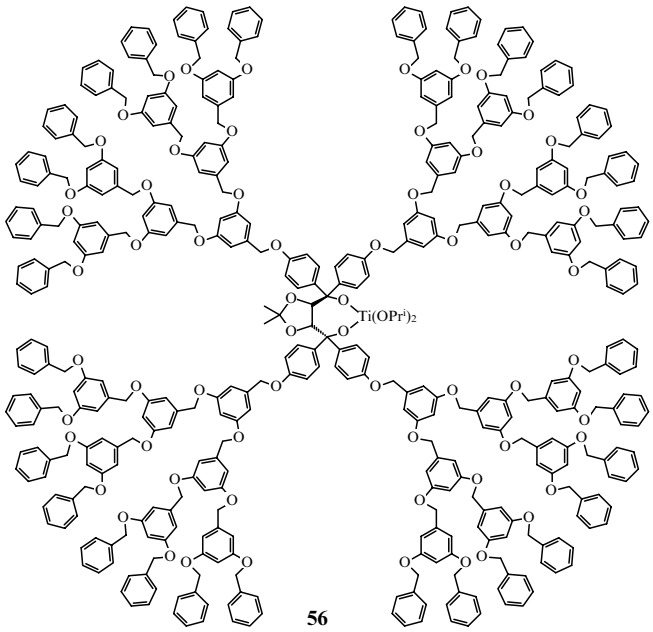
55

However, an attempt at using this compound as a starting material for the synthesis of a dendritic oxo-rhenium complex by conversion of the carbonyl groups, which could be used as a catalyst in oxidation reactions, was unsuccessful.

IX. Dendrimers containing central metal-containing fragments

The syntheses of dendrimers containing chiral titanium complexes in the centre of the molecule have recently been reported.[67,68] In these studies, (*R,R*)-α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) has been used as the core to which four dendrons prepared on the basis of 3,5-dihydroxybenzyl and/or octyl fragments were attached by the benzylation reaction.[67]

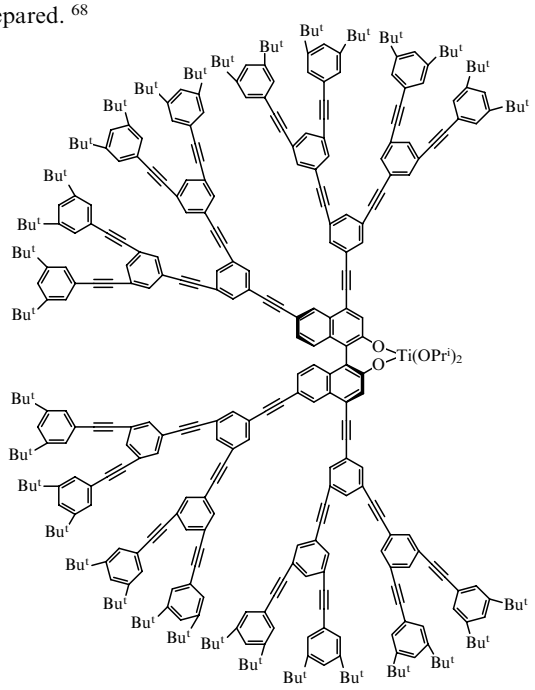
The catalytic activity of titanium complexes of the type **56** was studied in addition of diethylzinc to benzaldehyde. A slight



56

decrease in the catalytic activity and stereoselectivity with the increase in the number of dendrimer generations from zero to third was observed. However, on going to the fourth-generation dendrimers the decrease in the catalytic activity was more pronounced, being nearly two-fold. These results leave hope that second- and third-generation dendrimers can have possible applications as catalysts in membrane reactors.

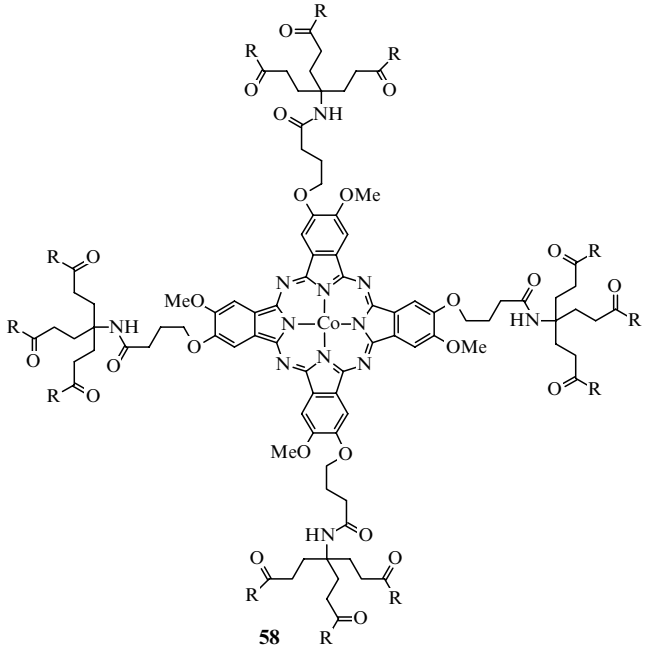
Analogously, dendrimers based on 1,3,5-triethynylbenzene with a central optically active 1,1′-bis(2-naphthol) fragment were prepared. [68]



57

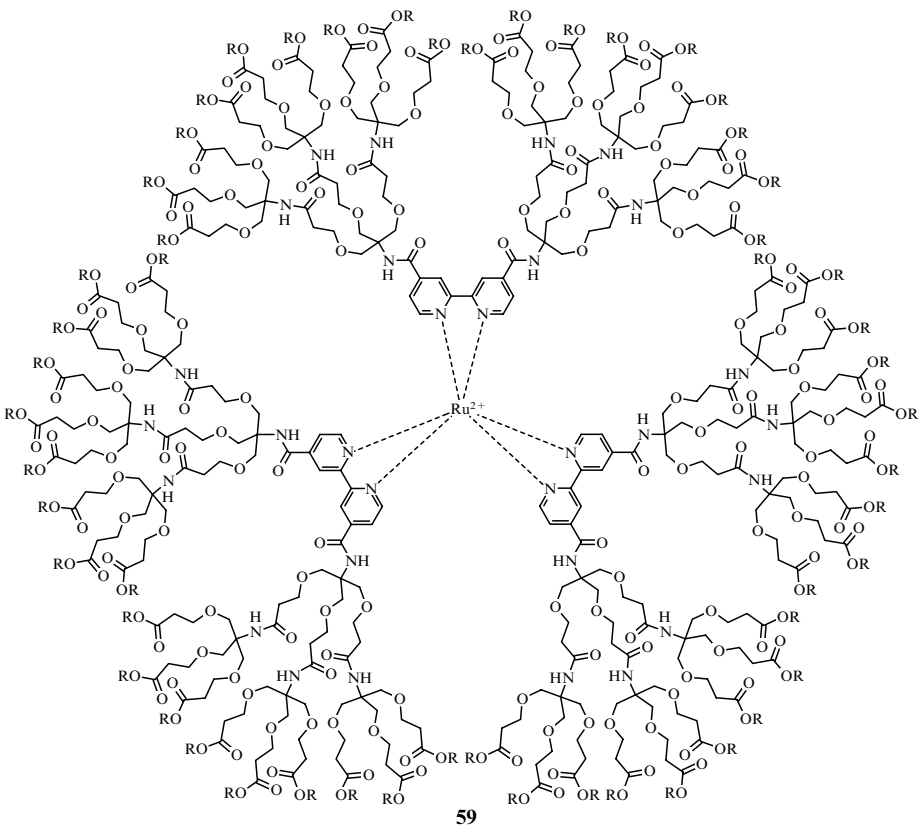
These dendrimers present special interest as chiral ligands and are used to recognise enantiomers. Catalytic activity of the titanium complex **57** was studied in the addition of diethylzinc to aldehydes, the enantiomeric excess attained being 89% – 90%. Yet another possible application of these dendrimers is the construction of a fluorescent probe for optical determinations of enantiomeric compositions of chiral compounds.

A dendrimer containing phthalocyanine as the central fragment and its cobalt complex **58** have been described.[69] Studies of the electrochemical properties of the dendrimer **58** showed that the dendritic shell prevents intermolecular interactions of the phthalocyanine fragments and thus impedes the electron transfer to the centre of the molecule. In the oxidation of 2-mercaptoethanol with oxygen, the catalytic activity of the dendrimer was 20%



58

R = $-NHC[CH_2CH_2CONHC(CH_2CH_2COOBu^t)_3]_3$.



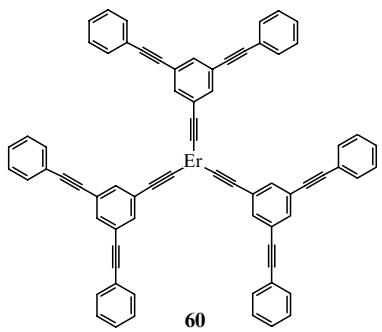
59

lower than that of the analogous non-dendritic phthalocyanine catalyst but its stability was higher in comparison with the latter.

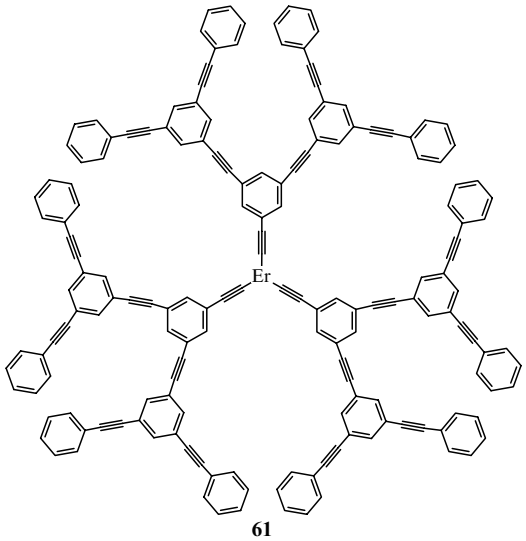
A great number of papers are devoted to the synthesis of dendrimers containing metal-porphyrin complexes as the central fragments. Such compounds present interest as selective oxidation catalysts mimicking enzymes.[70] The dendritic shell enhances the regioselectivity of the catalyst thus increasing its similarity to enzymes. In addition, such compounds were used in model studies of electron transfer in biological objects[71] and as fluorescent probes.[72]

Yet another possible application of dendrimers is the use of their shells as protectors for the cores. The ruthenium(II) complex **59** coordinated to three dendritic bipyridyl ligands provides an example.[73] It was shown that the lifetime of this complex in the excited state exceeds that of its non-dendritic analogue, since the dendritic shell protects the central part of the dendritic molecule from contacts with a solvent and dissolved oxygen and thus prevents luminescence quenching.

The organoerbium dendrimers of the first (**60**) and second (**61**) generations[74] were synthesised in the reaction of $Er[N(SiMe_3)_2]_3$ with phenylethynyl dendrons.



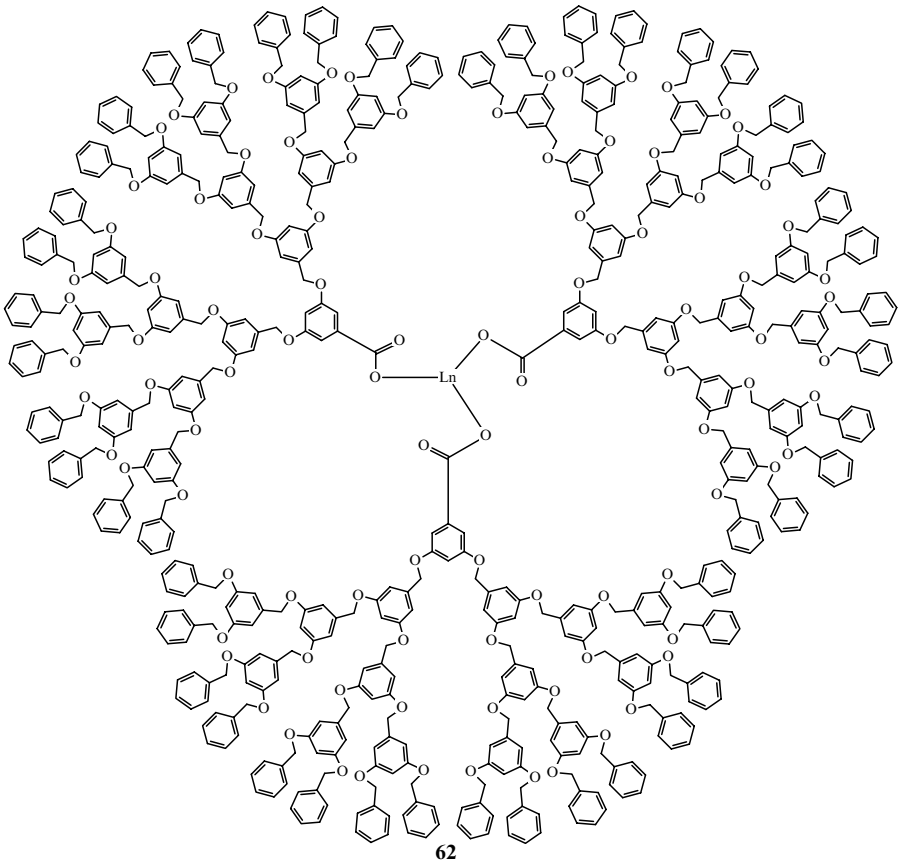
60



61

The starting phenylethynyl dendrons of the first and second generations were synthesised by using the convergent approach developed earlier for phenylethynyl dendrons with peripheral 3,5-di-*tert*-butylphenyl groups.[75] According to the computer simulation data, phenylethynyl dendrons represent rigid planar molecules which apparently do not provide sufficient shielding of the central erbium atom despite their considerable sizes. For example, the dendrimers **60** and **61** synthesised are as sensitive to atmospheric oxygen and moisture as other compounds of the organolanthanide series.[74]

Lanthanide derivatives are widely employed as luminophores.[76] However, the quantum yields of luminescence of lanthanide cations decrease as a result of cluster formation. In order to prevent luminescence quenching, lanthanide cations are encapsulated into a dendritic shell.[76,77] To this end, lanthanide triace-

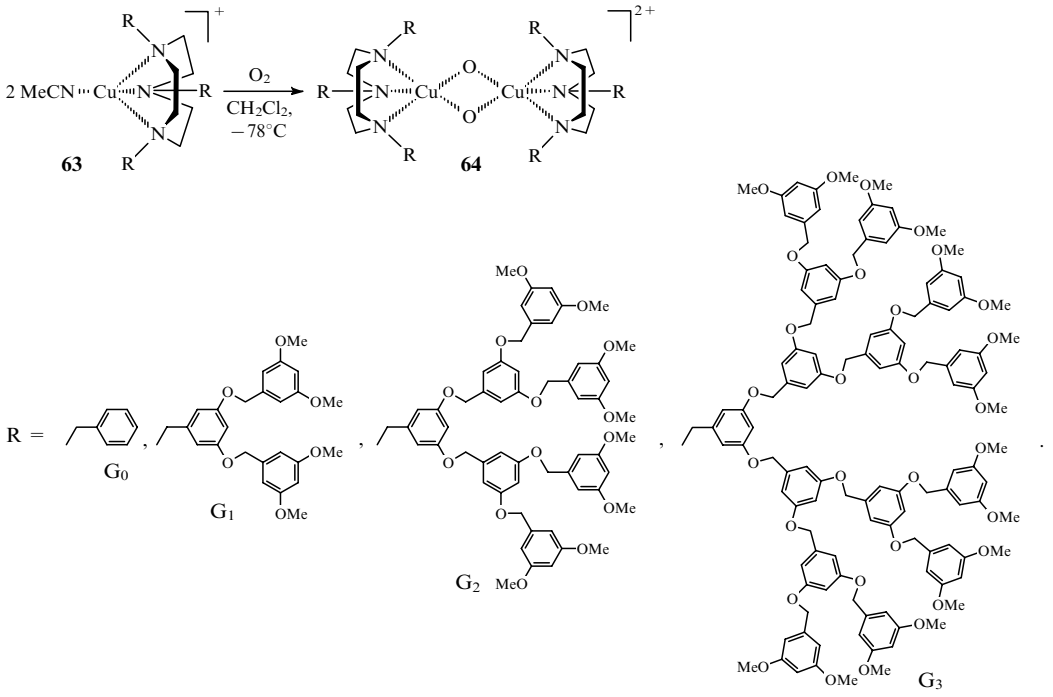


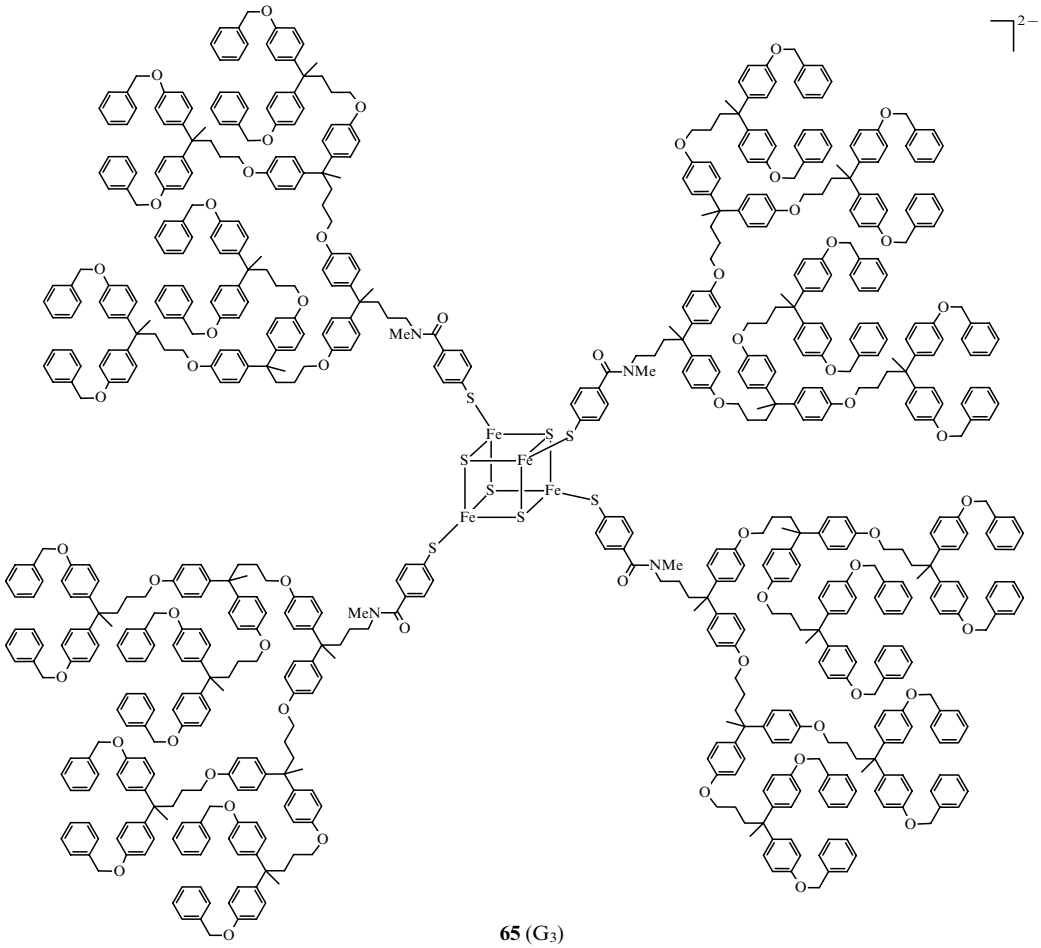
62

tates are introduced into a reaction with dendrons prepared on the basis of 3,5-dihydroxybenzyl fragments containing carboxy groups. The quantum yields of luminescence of the lanthanide complexes thus prepared (**62**) increased with the increase in the generation number for both solid samples and strongly diluted solutions of dendrimers in toluene. This effect can be attributed to the shielding of the lanthanide cations by dendritic ligands and the 'antenna effect', *i.e.*, the transfer of photoexcitation energy from the dendritic ligands to the lanthanide cations in the centre of the dendrimers despite the fact that dendrons based on 3,5-dihydroxybenzyl halides are not conjugated molecules.

Synthesis of a series of dendrimers of the first, second and third generations the nuclei of which represent monovalent copper complexes with 1,4,7-triazacyclononane have been described.[78] The rate constants for the oxidation of the dendritic complexes **63** synthesised with gaseous oxygen at −78 °C leading to the dendritic complexes **64** have been measured (Scheme 5). The oxidation rate constant for the second-generation dendrimer **63**

Scheme 5





65 (G_3)

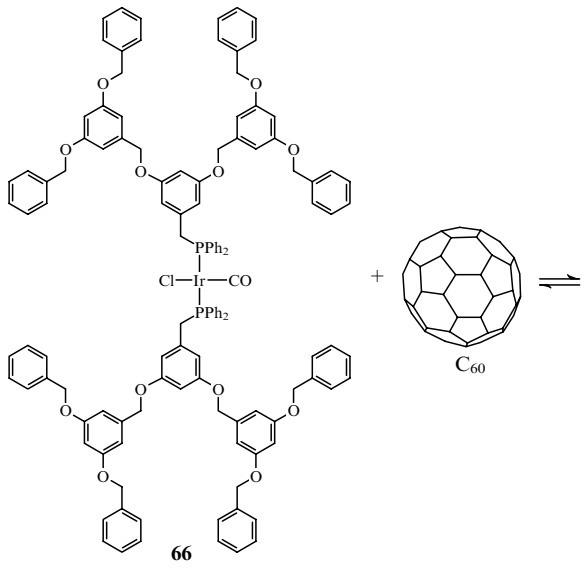
($R = G_2$), $k_2 = 1.3 \times 10^{-2}$ litre mol^{-1} s^{-1}, appeared to be two orders of magnitude lower than that of the first-generation dendrimer ($R = G_1$), $k_2 = 1.39$ litre mol^{-1} s^{-1}. The third-generation dendrimer ($R = G_3$) was resistant to oxidation under identical conditions.

With an increase in temperature to -10 °C, the complexes **64** are decomposed as a result of intramolecular oxidation with the cleavage of the C–N bond. The half-life of the non-dendritic complex **64** ($R = G_0$) is 7 s, whereas those of the first- ($R = G_1$) and second-generation ($R = G_2$) dendrimers are 24 and 3075 s, respectively, which seems to be due to steric hindrances in the transition state of the decomposition reaction created by the dendritic substituents. This opens a way to the synthesis of thermally stable bimetallic complexes mimicking the effects of enzymes.

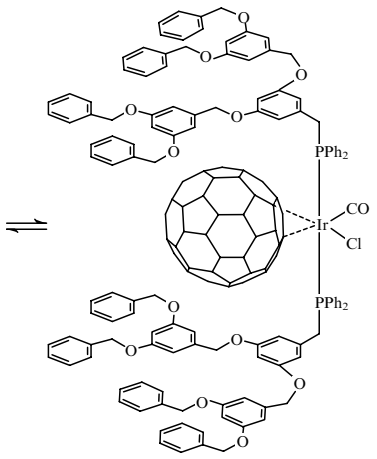
A method for encapsulation of noble metal microparticles in the core of polyamidoamine dendrimers (PAMAM) has been proposed.[79–81] To obtain such materials, Pd(II) or Pt(II) cations were adsorbed by a polyamidoamine dendrimer containing hydroxy groups in the centre of the molecule with subsequent reduction with $NaBH_4$.[79] Such dendrimers contain microparticles of noble metals in their central fragment and are readily soluble in water, which makes it possible to conduct organic reactions (*e.g.*, hydrogenation of alkenes) involving these species in the aqueous phase.[79] The solubility of such catalysts in non-polar solvents can be increased through the use of surfactants, *e.g.*, fatty acids, which form salts with the surface amine groups of the dendrimer.[80] The use of perfluorinated carboxylic acids in biphasic systems containing perfluorinated solvents presents special interest, since this allows easy separation of the catalyst from the reaction product after the termination of the reaction.[81]

Metallodendrimers of the zero, first, second, third and fourth generations which contain $Fe_4S_4(S_4^{2-})$ as the dendrimer core and can exist in two stable oxidation states, which can be used for storage of information, have been synthesised.[82] The dendritic shell in compound **65** prevents possible electron transfer between closely arranged molecules, which would result in the loss of stored information.[82] Voltammetric studies demonstrated that the electron transfer to the core of the molecule becomes more difficult with an increase in the number of the dendrimer generations.[82]

The iridium complex with dendritic phosphine ligands **66** was used for reversible binding of fullerene C_{60}.[83] The complex **66** was



66



prepared by the reduction of Na_3IrCl_6 with carbon monoxide with subsequent attachment of dendritic phosphine ligands. On addition of fullerene to the bright yellow solution of the dendrimer **66**, the solution of the dendrimer–fullerene complex changes its colour to dark green.

References

1. A M Muzafarov, E A Rebrov, V S Papkov *Usp. Khim.* **60** 1596 (1991) [*Russ. Chem. Rev.* **60** 807 (1991)]
2. M N Bochkarev, M A Katkova *Usp. Khim.* **64** 1106 (1995) [*Russ. Chem. Rev.* **64** 1035 (1995)]
3. J-P Majoral, A-M Caminade *Chem. Rev.* **99** 845 (1999)
4. M A Hearshaw, J R Moss *Chem. Commun.* 1 (1999)
5. A Archut, F Vögtle *Chem. Soc. Rev.* **27** 233 (1998)
6. H-F Chow, T K-K Mong, M F Nongrum, C-W Wan *Tetrahedron* **54** 8543 (1998)
7. C Gorman *Adv. Mater.* **10** 295 (1998)
8. H W I Peerlings, E W Meijer *Chem. Eur. J.* **3** 1563 (1997)
9. G van Koten, J T B H Jastrzebski *J. Mol. Catal. A.* **146** 317 (1999)
10. F J Stoddart, T Welton *Polyhedron* **18** 3575 (1999)
11. M Fischer, F Vögtle *Angew. Chem., Int. Ed. Engl.* **38** 884 (1999)
12. I Cuadrado, M Morán, C M Casado, B Alonso, J Losada *Coord. Chem. Rev.* **193–195** 395 (1999)
13. M Osawa, H Sonoki, M Hoshino, Y Wakatsuki *Chem. Lett.* 1081 (1998)
14. M Osawa, M Hoshino, S Horiuchi, Y Wakatsuki *Organometallics* **18** 112 (1999)
15. D Tzalis, Y Tor *J. Chem. Soc., Chem. Commun.* 1043 (1996)
16. Z Xu, J S Moore *Acta Polym.* **45** 83 (1994)
17. S Takahashi, Y Kuroyama, K Sonogashira, N Hagihara *Synthesis* 627 (1980)
18. C Devadoss, P Bharathi, J S Moore *J. Am. Chem. Soc.* **118** 9635 (1996)
19. Z Zhu, J S Moore *J. Org. Chem.* **65** 116 (2000)
20. T Kaneko, T Horie, M Asano, T Aoki, E Oikawa *Macromolecules* **30** 3118 (1997)
21. S Kotha, K Chakraborty, E Brahmachary *Synlett* 1621 (1999)
22. E C Constable, C E Housecroft, B Krattinger, M Neuburger, M Zehnder *Organometallics* **18** 2565 (1999)
23. N Ohshiro, F Takei, K Onitsuka, S Takahashi *J. Organomet. Chem.* **569** 195 (1998)
24. A M McDonagh, M G Humphrey, M Samoc, B Luther-Davies *Organometallics* **18** 5195 (1999)
25. W T S Huck, F C J M van Veggel, D N Reinhoudt *Angew. Chem., Int. Ed. Engl.* **35** 1213 (1996)
26. W T S Huck, L J Prins, R H Fokkens, N M M Nibbering, F C J M van Veggel, D N Reinhoudt *J. Am. Chem. Soc.* **120** 6240 (1998)
27. I P Beletskaya, A V Chuchurjukin, H P Dijkstra, G P M van Klink, G van Koten *Tetrahedron Lett.* **41** 1075 (2000)
28. I P Beletskaya, A V Chuchurjukin, H P Dijkstra, G P M van Klink, G van Koten *Tetrahedron Lett.* **41** 1081 (2000)
29. I P Beletskaya, A V Chuchurjukin, I L Eremenko, H P Dijkstra, G van Klink, G van Koten *J. Organomet. Chem.* (2000) (in the press)
30. W T S Huck, B Snellink-Ruel, F C J M van Veggel, D N Reinhoudt *Organometallics* **16** 4287 (1997)
31. A W Kleij, H Kleijn, J T B H Jastrzebski, W J J Smeets, A L Spek, G van Koten *Organometallics* **18** 268 (1999)
32. J W J Knapen, A W van der Made, J C de Wilde, P W N M van Leeuwen, P Wijkens, D M Grove, G van Koten *Nature (London)* **372** 659 (1994)
33. M Albrecht, R A Gossage, A L Spek, G van Koten *Chem. Commun.* 1003 (1998)
34. M Albrecht, R A Gossage, M Lutz, A L Spek, G van Koten *Chem. Eur. J.* **6** 1431 (2000)
35. M Bardaji, A -M Caminade, J-P Majoral, B Chaudret *Organometallics* **16** 3489 (1997)
36. M Bardaji, M Kustos, A-M Caminade, J-P Majoral, B Chaudret *Organometallics* **16** 403 (1997)
37. P Lange, A Schier, H Schmidbaur *Inorg. Chem.* **35** 637 (1996)
38. P Lange, A Schier, H Schmidbaur *Inorg. Chim. Acta* **235** 263 (1995)
39. K Kollner, B Pugin, A Togni *J. Am. Chem. Soc.* **120** 10274 (1998)
40. A Togni *Angew. Chem., Int. Ed. Engl.* **35** 1475 (1996)
41. D de Groot, E B Eggeling, J C de Wilde, H Kooijman, R J van Haaren, A W van der Made, A L Spek, D Vogt, J N H Reek, P C J Kamer, P W N M van Leeuwen *Chem. Commun.* 1623 (1999)
42. S C Bourque, F Maltais, W-J Xiao, O Tardif, H Alper, P Arya, L E Manzer *J. Am. Chem. Soc.* **121** 3035 (1999)
43. S C Bourque, H Alper *J. Am. Chem. Soc.* **122** 956 (2000)
44. V Balzani, S Campagna, G Denti, A Juris, S Serroni, M Venturi *Acc. Chem. Res.* **31** 26 (1998)
45. E C Constable, A M W Cargill Thompson *J. Chem. Soc., Dalton Trans.* 3467 (1992)
46. E C Constable, A M W Cargil Thompson, P Harveson, L Macko, M Zehnder *Chem. Eur. J.* **1** 360 (1995)
47. G R Newkome, F Cardullo, E C Constable, C N Moorefield, A M W Cargill Thompson *J. Chem. Soc., Chem. Commun.* 925 (1993)
48. E C Constable, P Harverson *J. Chem. Soc., Chem. Commun.* 33 (1996)
49. E C Constable, P Harverson *Inorg. Chim. Acta* **252** 9 (1996)
50. E C Constable, P Harverson, M Oberholzer *J. Chem. Soc., Chem. Commun.* 1821 (1996)
51. D Armspach, M Cattalini, E C Constable, C E Housecroft, D Philips *J. Chem. Soc., Chem. Commun.* 1823 (1996)
52. G R Newkome, A K Patri, L A Godinez *Chem. Eur. J.* **5** 1445 (1999)
53. C J Hawker, J M J Frechet *J. Am. Chem. Soc.* **112** 7638 (1990)
54. Y-H Liao, R Moss *Organometallics* **15** 4307 (1996)
55. N J Hovestad, J L Hoare, J T B H Jastrzebski, A J Canty, W J J Smeets, A L Spek, G van Koten *Organometallics* **18** 2970 (1999)
56. S Achar, J J Vittal, R J Puddephatt *Organometallics* **15** 43 (1996)
57. S Achar, R J Puddephatt *Angew. Chem., Int. Ed. Engl.* **33** 847 (1994)
58. G-X Liu, R J Puddephatt *Organometallics* **15** 5257 (1996)
59. I Cuadrado, C Casado, B Alonso, M Moran, J Losada, V Belsky *J. Am. Chem. Soc.* **119** 7613 (1997)
60. J-L Fillaut, J Linares, D Astruc *Angew. Chem., Int. Ed. Engl.* **33** 2460 (1994)
61. R Castro, I Cuadrado, B Alonso, C M Casado, M Moran, A E Kaifer *J. Am. Chem. Soc.* **119** 5760 (1997)
62. S Achar, C E Immoos, M G Hill, V J Catalano *Inorg. Chem.* **36** 2314 (1997)
63. C Valerio, J L Fillaut, J Ruiz, J Guittard, J-C Blais, D Astruc *J. Am. Chem. Soc.* **119** 2588 (1997)
64. F Lobete, I Cuadrado, C M Casado, B Alonso, M Moran, J Losada *J. Organomet. Chem.* **509** 109 (1996)
65. K Brüning, H Lang *J. Organomet. Chem.* **592** 147 (1999)
66. I J Mavunkal, J R Moss, J Bacsa *J. Organomet. Chem.* **593–594** 361 (2000)
67. P B Rheiner, D Seebach *Chem. Eur. J.* **5** 3221 (1999)
68. Q -S Hu, V Pugh, M Sabat, L Pu *J. Org. Chem.* **64** 7528 (1999)
69. M Kimura, Y Sugihara, T Muto, K Hanabusa, H Shirai, N Kobayashi *Chem. Eur. J.* **5** 3495 (1999)
70. P Bhyrappa, J K Young, J S Moore, K S Suslick *J. Am. Chem. Soc.* **118** 5708 (1996)
71. P J Dandliker, F Diederich, J-P Gisselbrecht, A Louati, M Gross *Angew. Chem., Int. Ed. Engl.* **34** 2725 (1995)
72. R Sadamoto, N Tomioka, T Aida *J. Am. Chem. Soc.* **118** 3978 (1996)

73. J Issberner, F Vögtle, L De Cola, V Balzani *Chem. Eur. J.* **3** 706 (1997)
74. M N Bochkarev, M A Katkova, S Ya Khorshev, N P Makarenko *Izv. Akad. Nauk, Ser. Khim.* 356 (1998) [a]
75. Z Xu, M Kahr, K L Walker, C L Wilkins, J S Moore *J. Am. Chem. Soc.* **116** 4537 (1994)
76. M Kawa, J M J Fréchet *Thin Solid Films* **331** 259 (1998)
77. M Kawa, J M J Fréchet *J. Chem. Mater.* **10** 286 (1998)
78. M Enomoto, T Aida *J. Am. Chem. Soc.* **121** 874 (1999)
79. M Zhao, R M Crooks *Angew. Chem., Int. Ed. Engl.* **38** 364 (1999)
80. V Chechik, M Zhao, R M Crooks *J. Am. Chem. Soc.* **121** 4910 (1999)
81. V Chechik, R M Crooks *J. Am. Chem. Soc.* **122** 1243 (2000)
82. C B Gorman, B L Parkhurst, W Y Su, K-Y Chen *J. Am. Chem. Soc.* **119** 1141 (1997)
83. V J Catalano, N Parodi *Inorg. Chem.* **36** 537 (1997)

[a] — *Russ. Chem. Bull. (Engl. Transl.)*