Large Transition Metal Clusters, 2 [1]. Synthesis and Properties of $Rh_{55}[P(tert-Bu)_3]_{12}Cl_{20}$

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The reaction of a mixture of [(tert-Bu)₃P]₂Rh-(H₂)Cl and [(tert-Bu)₃P]₂Rh(CO)Cl with gaseous diborane in benzene solutions at 50–60 °C leads to a cluster whose formula is assumed to be Rh₅₅[P(tert-Bu)₃]₁₂Cl₂₀, due to analytical, spectroscopic, and chemical results. The number 55 is one of the 'magic numbers' of full shell cuboctahedrons or icosahedrons. ³¹P, and ¹⁰³Rh N.M.R. investigations assign a high mobility either of the ligands or of the rhodium atoms or of both.

The coordinatively unsaturated surface of the cluster whose structure is supposed to be cuboctahedral, allows gaseous carbon monoxide to be adsorbed irreversibly, even if the cluster is in the solid state. The CO groups are coordinated exclusively in a terminal manner.

Introduction

The problem of the mechanism of nucleation and structure of clusters and very small crystallites has often been the subject of different patterns and calculations. The increasing effort for a better understanding of the facts in heterogeneous catalysis has led to different and partially contradictory views on the growth and structure of clusters and microcrystallites. There exist concrete and plausible conceptions describing different pathways of nucleation, *viz.* pentagonal, tetrahedral, or icosahedral growth [2]. All kinds of nucleations may start with a tetrahedron whose formation is trivial and to whom further atoms can be attached in a different manner. So, the formation of a 55 atom cluster can be postulated with the tetrahedron first growing to a trigonal bipyramid, followed by expansion to a pentagonal bipyramid, a 13 atom icosahedron, then to a 33 atom dodecahedron, and finally to a 55 atom icosahedron [3].

Opinions on the stability of full shell clusters (icosahedron, cuboctahedron) differ: those geometries which are signed by 'magic numbers' like 13, 55, 147 (in general $10n^2 + 2$ per nth layer) are described either as non-existing [4, 5] or not observable [6]. On the contrary 'polytetrahedral' structures are preferred [4, 7, 8]. As an exception the 55 atom icosahedron is described as having a greater bond energy than any other known 'polytetrahedral' structure [7]. Close-packed clusters with cuboctahedral arrangements are considered unstable (in principle) compared with icosahedral structures [3, 7, 9, 10]. Therefore the surfaces of very small microcrystallites possess predominantly (111) planes but not (100) faces [3]. Only in the bulk lattice, cubic or hexagonal close-packed structures exist. These results, based on mathematical and physical concepts, can be only partially accepted for chemical problems. To synthesize and to isolate large clusters, chemical effects may influence physically known stabilities or instabilities, but the 'prohibition of magic numbers' for 'naked clusters' is to be doubted as the special stability of the 'magic numbers' 13, 55 and 147 resp. has recently been demonstrated experimentally on xenon clusters [11]. Cuboctahedral and icosahedral structures for 13-atom clusters are well known, if they are stabilized chemically by coordination of ligands. Thus, we find a twisted cuboctahedral structure for $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ [12] and an icosahedral arrangement for $Au_{13}(diphos)_2]^{4+}$ [13].

It is to be supposed that the individual details, especially the kind and number of ligands, determine if a cuboctahedral (ccp), a twisted cuboctahedral (hcp), or an icosahedral structure will be verified. There is a strong relationship between ccp and hcp structures. Both exist in metals, the hcp arrangement having a less dense packing than the ccp structure. On the other hand, cuboctahedrons and icosahedrons also show a very close relationship, as each can be transformed into its counterpart by simple rotation of their triangular faces about the normal [14].

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Icosahedral packing becomes more unlikely with increasing numbers of atoms [15].

Recently we reported the largest isolated metal cluster of molecular behaviour up to that time, Au_{55}-$(PPh_3)_{12}Cl_6$ [1]. The synthetic and structural concepts developed for the Au_{55} cluster should also hold for other transition metals. The favored formation of 55 atom clusters has been postulated by the theoretical calculations mentioned above [7]. We have found that an arrangement of 12 phosphines and 6 chlorine ligands on the cluster surface is more feasible for a cuboctahedron than an icosahedron with 20 equivalent trigonal faces.

The fact that most of the larger clusters synthesized by other workers deviate in the number of atoms from 13 and 55 can probably be substantiated by the methods of preparation, normally based on the stepwise increasing or decreasing of existing clusters [12].

'Magic numbers' in a chemically realistic region, i.e. 13 and 55, should be realized if metal atoms come together unhindered, e.g. by the condensation of metal vapor or by chemical formation in solution. Which of the 'magic numbers' will be realized in solution depends mainly on the nature and the concentration of the ligands. Of particular importance is the shielding effect by the ligand which creates a 'plane of coverage' over the metal atoms. In this respect triphenylphosphine proved to be very effective for the Au_{55} cluster. The chlorine atoms occupy the interstices not being covered by the phosphines. The extent to which positive charge on the metal atoms caused by the halogen atoms is important for cluster stability cannot be estimated at this time.

Besides the geometry of the ligands their concentration plays a decisive role during cluster synthesis. A special importance is due to diborane: on the one hand it serves as a reducing agent to the metal halide, on the other it acts as a Lewis acid to free phosphine. Too high phosphine concentrations would favor the formation of smaller clusters or lead to decomposition of larger clusters [16]. Ligand concentrations which are too low would give rise to metal formation. Therefore the position of the equilibrium

$$B_2H_6 + 2PR_3 \rightleftharpoons 2H_3B-PR_3$$
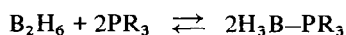
is essential as the concentration on free phosphine is determined by it.

We have transformed the model discussed in detail for $Au_{55}(PPh_3)_{12}Cl_6$ [1] to the element rhodium and have selected the tri-tert-butylphosphine besides chlorine as ligands because of the geometrical facts on a supposed Rh_{55} cuboctahedron surface.

Results

Preparation of $Rh_{55}[P(tert-Bu)_3]_{12}Cl_{20}$

A rhodium complex of the type $[(tert-Bu)_3P]_n$-RhCl would be most suitable for reduction by di-

borane. Experiments to prepare a compound of this type by reaction of $RhCl_3 \cdot 3H_2O$ with $P(tert-Bu)_3$ in ethanol yielded a mixture of $[(tert-Bu)_3P]_2Rh(H_2)$-Cl, 1 [17] and $[(tert-Bu)_3P]_2Rh(CO)Cl$, 2 [18] which could not be separated quantitatively.

Therefore, we used the original mixture of 1 and 2 for the reaction with B_2H_6, as 2 reacts in the same manner as 1.

A solution of the mixture of 1 and 2 (approx. 1:1) reacts with gaseous B_2H_6 at 50–60 °C during 60–90 min to produce a dark reaction mixture from which brown-black pyrophoric $Rh_{55}[P(tert-Bu)_3]_{12}Cl_{20}$, 3, can be isolated in 80% yield. 3 is slightly soluble in THF, pyridine or benzene but is more soluble in acetone or diacetone alcohol. In acetone and diacetone alcohol, however, partial decomposition may occur (see ^{31}P NMR spectra) leading to products of unknown nature.

Physical Investigations

Molecular weight determination

A conclusive determination of the cluster size was made due to a molecular weight determination of 3. We determined the molecular weight to be 9000 ± 500 (calcd. 8796.7) in an acetone solution by means of sedimentation measurements with an analytical ultracentrifuge, as previously described for the Au_{55} cluster [1]. Although this value is within the accuracy of this type of measurement, it may be too high due to strong interactions between 3 and the solvent.

NMR measurements

The [31]P–{[1]H} spectrum of 3 in acetone solution shows only one sharp singlet at 68 ppm, whereas in the non spin-decoupled spectrum the signal consists of a multiplet caused by ^{31}P–C–C–[1]H couplings with $^3J(P-H) \approx 10$ Hz as in free $P(tert-Bu)_3$. Accompanying this singlet there are some smaller signals resulting from decomposition and reactions with the solvent. The strongest signal of the decomposition products at 55 ppm is a doublet with $^1J(P-H) = 450$ Hz (± 15 Hz) due to an unknown compound formed by reaction with acetone. Using d_6-acetone as solvent, a triplet with $^1J(P-D) = 70$ Hz is observed, demonstrating that the hydrogen bound to phosphorus originates from the solvent. Some free $P(tert-Bu)_3$ is indicated by a signal at 62.5 ppm. We are still not able to explain the origin of the signal at 55 ppm, but possibly it is due to a phosphonium salt.

The same results are obtained using diacetone alcohol as a solvent instead of acetone. Referring to 3, the signal at 68 ppm lacks the expected [31]P–[103]Rh coupling but is comparable with that of the analogous ruthenium cluster $Ru_{55}[P(tert-Bu)_3]_{12}$-$Cl_{20}$ at 67 ppm [19]. It has been shown that clusters of different types possess scrambling ligands. The

mobility of the CO groups in *e.g.* $Rh_4(CO)_{12}$ was proven by ^{13}C-NMR experiments [20, 21] by the observation of the spectrum at -65 °C, consisting of 4 lines which are split to a doublet caused by [13]C–[103]Rh coupling. Above $+50$ °C the spectrum is characterized by a fast chemical exchange and shows a quintet. The coalescence temperature is -5 ± 5 °C. The ^{31}P NMR spectrum of the rhodium cluster Rh_{13}-$[P(OMe)_3]_8Cl_4$ [22] suggests a very similar behaviour of the phosphines. At -50 °C only a very weak signal is present, but at 25 °C a broad singlet can be observed, demonstrating an intramolecular ligand exchange. The extreme case of the fast chemical exchange, a sharp singlet, could not be reached by further warming of the sample as the cluster decomposed. However this limiting case $|J(^{31}P, ^{103}Rh)| \cdot \tau \ll 1$ (τ is the longest lifetime of any site of the cluster) is realized in the large cluster *3* whose ^{31}P NMR spectrum shows a sharp singlet with a completely averaged coupling. This singlet indicates a fast exchange of the phosphine ligands relative to the cluster surface.

[103]Rh NMR investigations should give more information on the cluster nucleus. Using a spectrometer especially developed for nuclei with weak NMR signals [23], we tried to record the [103]Rh NMR spectrum of *3*. To this end we used about 15 ml of a 0.002 molar solution of *3* in diacetone alcohol in a tube with an inner diameter of 20 mm. To detect the unknown [103]Rh resonances the Quadriga technique [24] was applied: this builds up a steady-state in the nuclear spin system and through it a continuous NMR signal during the whole measuring time is obtained. Compared with the most commonly applied technique, to observe the decay of the free induction and to await thermal equilibration before successive pulses, the Quadriga technique achieves a higher signal/noise ratio by the factor $(T_2/T_2^*)^{1/2}$ [25] during the same measuring time, where T_2^* is the decay time constant due to the inhomogeneity of the field B_0.

In search of the unknown [103]Rh spectrum, a maximum repetition rate of 166 Hz was applied for the periodic, equal and coherent pulses to be irradiated. To begin with, rf pulses with the flip angle $\theta = 50°$ were irradiated, yielding an optimum NMR signal for nuclei with a ratio of the relaxation times $T_1/T_2 = 5$. As the search with this flip angle did not result in a [103]Rh NMR signal, the measurement was repeated with pulses of the flip angle $\theta = 25°$ which are optimal for nuclei with $T_1/T_2 = 20$.

In a field $B_0 = 2.114$ T (corresponding to a proton resonance frequency of 90 MHz) the frequency range from 2.830 to 2.870 MHz was scanned for the unknown [103]Rh spectrum of *3*. This frequency range corresponds to a chemical shift range of $\delta = -5000$ to $+9000$ ppm relative to the fictitious standard with the ratio for the resonance frequences $\nu^{103}Rh/\nu^1H$-

(TMS) $= 0.0316$, proposed by Garth Kidd and Goodfellow [26]. In this region all [103]Rh resonances which have been detected up to now [26, 27] are found, in particular the resonance of metallic rhodium [28], as well as the resonances of a rhodium cluster [29].

We were not able to find a [103]Rh NMR signal in that region for the rhodium cluster *3*. It must be assumed that this negative result is due to a very unfavorable (*i.e.* high) ratio of relaxation times T_1/T_2, as the [103]Rh resonance can be excluded beyond the mentioned range of frequencies. The sensitivity of the spectrometer employed is well known from a previous series of [103]Rh investigations [27]. On the supposition that the nucleus of *3* consists of a two shell cuboctahedron (or icosahedron) and that the 12 Rh atoms of the first shell, surrounding the central Rh atom, and also the 42 Rh atoms of the second shell have the same [103]Rh resonance frequency (the sample is 24 mmolar and 84 mmolar in Rh atoms of the first and second shell respectively) the Rh resonance of the first shell up to a ratio $T_1/T_2 < 6$ and the resonance of the second shell up to $T_1/T_2 < 70$ should be detectable.

The [103]Rh relaxation is due to a fast fluctuating anisotropic chemical shift in all known cases [27], *i.e.* to a relaxation mechanism with a ratio T_1/T_2 close to 1 [30]. A drastic shortening of the transverse relaxation time T_2, and thus an increase of the ratio T_1/T_2, has been observed if the resonance frequency of the investigated Rh nuclei shows a fluctuation. If the Fourier transform spectrum of this fluctuation contains mainly frequencies above the [103]Rh Larmor frequency ν_L, *i.e.* the condition $\nu_L \cdot \tau \ll 1$ is fulfilled (τ is the lifetime of the longest-lived site), the fluctuation effects on the longitudinal as well on the transverse relaxation, and the ratio T_1/T_2 remains constant. But if the Fourier transform spectrum of the fluctuation contains a considerable intensity below the Larmor frequency, *i.e.* the condition $\nu_L \cdot \tau \gtrsim 1$ holds, then the fluctuation effects are mainly on the transverse relaxation, leading to an increase of T_1/T_2.

Such a fluctuation of the [103]Rh Larmor frequency can be caused by

1) chemical exchanges in the cluster, leading to a change in chemical shift of the [103]Rh nuclei under investigation,

2) a scalar coupling of the [103]Rh nuclei with another magnetic nucleus. Such a scalar coupling would not contribute to a decrease of T_2 if

a) the coupling is very small compared with the pulse repetition frequency used in the method of measurement: $|J| \ll 166$ Hz or,

b) the coupling nucleus is subjected to a very fast chemical exchange (main intensity of the Fourier transform spectrum of this exchange above the [103]Rh Larmor frequency: $\nu_L \cdot \tau \ll 1$) through which coupling is averaged.

A chemical reaction at the Rh cluster, which would occur very slowly compared with the longitudinal relaxation time T_1, does not destroy the steady state; possibly the ^{103}Rh spectrum could show signals of the starting compound and of the reaction product.

For $Rh_{13}[P(OMe)_3]_8Cl_4$ as for 1 the ^{103}Rh–^{31}P coupling was observed by ^{31}P NMR. 1 showed a resolved doublet whereas the Rh_{13} cluster gave a signal broadened by coalescence due to chemical exchange. The sharp ^{31}P signal in the spectrum of 3 shows that the exchange has become so fast that $\tau \cdot \Delta\nu(^{31}P) \ll 1$ is valid for the life-time τ of the longest-lived exchange state, where $\Delta\nu(^{31}P)$ is the largest difference of the ^{31}P Larmor frequencies in the various exchange states due to the ^{31}P–^{103}Rh coupling and to the different chemical environment.

The influence of a ^{31}P–^{103}Rh scalar coupling with a coupling constant $|J(^{31}P–^{103}Rh)| = 80$ to 200 Hz on the ratio T_1/T_2 can not be eliminated by the steady-state technique, using a high pulse repetition rate as described above in (2a). Instead a rather drastic decrease of the transverse relaxation time T_2 will result, i.e. $T_1/T_2 \gg 1$, if τ is not short compared with the ^{103}Rh Larmor period as mentioned in (2b). So the disappearance of the ^{103}Rh spectrum yields a lower limit for the life-time of the longest-lived exchange states: $\tau > 10^{-7}$ sec.

The ^{31}P and ^{103}Rh experiments result in the following consequences: the phosphorus and the rhodium atoms of the cluster change continuously their positions relative to each other, e.g. either the P or the Rh atoms or both species are in motion. Similar observations have been made for $[Rh_9P(CO)_{21}]^{2-}$ [29]. Furthermore it may be of interest that from a physical point of view clusters with approx. 50 metal atoms are believed to have the liquid-like behaviour of the surface atoms [2]. From the behaviour of the ^{31}P resonance (singlet due to the fast chemical exchange) it can be concluded that the life-time of the longest-lived exchange state is: $\tau \ll 1/\Delta\nu(^{31}P)$.

On the other hand the disappearance of the ^{103}Rh resonance due to the high T_1/T_2 value leads to the conclusion: $\tau \gtrsim 1/\nu_L(^{103}Rh) \approx 10^{-7}$ sec.

It thus appears that the representation of a definite surface structure of 3 in solution is impossible. An exchange mechanism cannot be discussed as yet, but can be easily understood in terms of molecular rearrangements within the structure to give a cubic, hexagonal, or icosahedral array of atoms. It now becomes possible to understand why we were not able to get visible crystals from solution. In the mobile, entropically-favored system, any number of states may exist, preventing formation of macroscopic crystals. On the other hand, it must be assumed that in the amorphous or microcrystalline powders, the best arrangements of Rh atoms and of the ligands are verified by attaching the highest probability to a cuboctahedral structure, as in the Au_{55} case.

Comparing $Au_{55}(PPh_3)_{12}Cl_6$ with $Rh_{55}[P(tert-Bu)_3]_{12}Cl_{20}$, 3, the higher yield on halogen for 3 attracts attention. The molecular models show that in the case of a cuboctahedral arrangement of the 55 metal atoms, the 12 vertices are occupied by the phosphines and there is indeed space enough for 20 chlorine atoms. Each triangular face may be coordinated by one, and each square face by two chlorine atoms (see Fig. 1) forming bridges between two or three Rh atoms. The reason why the Au_{55} cluster contains only 6 chlorine ligands can be understood in terms of the much lower reactivity of gold as compared to rhodium.

Chemical Properties

The model as well as the reactivity of 3 demonstrate that the cluster surface must still be coordinatively unsaturated. 3 reacts spontaneously with atmospheric oxygen and also with carbon monoxide. As can be seen from Fig. 1, there are still 6 distinguishable Rh atoms in the centres of the squares which are available for interaction with small molecules. To avoid any participation of solvent molecules as well as dissociation of phosphines, a solid sample of 3 is exposed to CO gas at about 1 atm of pressure. There is a very fast and irreversible adsorption of 6 molecules of CO per molecule of 3. The reaction can easily be followed quantitatively by volumetric measurements. The adsorbed CO cannot be lost under vacuum and causes one intensive, broad $\nu(CO)$ band in the IR spectrum at 2010 cm^{-1}, proving the terminal character of the coordinated CO groups. In the region of bridging CO groups there are no absorptions to be recognized. The number as well as the terminal character of the CO ligands support a cuboctahedral structure corresponding to Fig. 1. The six Rh atoms in the centres of the six squares are the only positions where CO ligands can be fixed terminally.
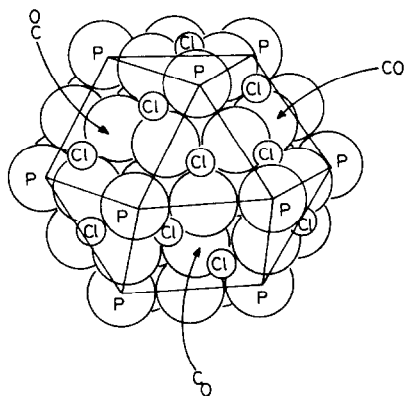

Fig. 1. The proposed structure for 3. The arrows point to the positions where CO molecules may be coordinated. The phosphine and chlorine ligands are omitted and only indicated for clarity.

The physical and chemical properties of *3* should make it a potential and versatile catalyst. Initial investigations on the hydrogenation, hydroformylation, and isomerization of alkenes seem to confirm this. Current research indicates that other transition metals like ruthenium, nickel, and platinum form analogous clusters. It is also confirmed in all cases that the structure of the ligands used must be suited to the size of the metal.

Experimental

All reactions and measurements were carried out in freshly distilled, dry, nitrogen-saturated solvents. Microanalyses were performed by the Analytical Laboratory in the Institute for Inorganic Chemistry, University of Essen and by Dornis and Kolbe, Mülheim/Ruhr. The ^{31}P NMR spectra were recorded on a Varian XL 200 spectrometer; IR spectra were obtained with Perkin Elmer 283 B and 597 spectrometers. The determination of the molecular weight was performed according to the procedure described earlier [1], using an analytical ultracentrifuge Spinco Modell E (Beckmann) and a densimeter DMA 50 (Heraeus-Paar). The spectrometer used for the ^{103}Rh NMR measurements has been described previously [23].

Preparation of $Rh_{55}[P(tert-Bu)_3]_{12}Cl_{20}$, 3

1.9 g of a mixture of *1* and *2* (3.4 mmol on the supposition of a 1:1 mixture), dissolved in 100 ml of benzene, were reacted with a slow stream of B_2H_6 [1] (from 30 g $NaBH_4$ and 150 ml BF_3-etherate) at 50–60 °C over 60–90 min. using a 250 ml three-necked flask equipped with a stirrer, a gas distribution tube, a reflux condenser, and an inside thermometer. The solution darkened and gave a brownish-black reaction mixture. After diborane formation, the flask was cooled down to room temperature and all volatile materials were pumped off. The residue was washed several times with petroleum ether and with a little benzene to remove all H_3B-$P(tert-Bu)_3$. This could be confirmed in IR spectroscopy by the absence of any B–H frequencies in the region of 2400–2500 cm^{-1}. To prevent dissociation of P(tert-Bu)$_3$ from the cluster it is helpful to add some drops of the phosphine to the benzene. Isolation of *3* by this method may give samples with traces of rhodium metal. For further purification, the product may be dissolved in acetone, and after filtration *3* can be isolated by evaporation of the solvent. This procedure should be finished as soon as possible to avoid decomposition in solution. Yield: 0.45 g *3* (82.6%). *Anal.* Calcd. for $C_{144}H_{324}Cl_{20}P_{12}Rh_{55}$: C, 19.67; H, 3.71; Cl, 8.06; P, 4.22; Rh, 64.34. Found: C, 19.80; H, 4.10; Cl, 8.4; P, 4.0; Rh, 63.35.

Reaction of 3 with CO

Two flasks F_1 and F_2 as parts of a high-vacuum line were linked together by a connecting cock. The total volume was 935.22 ml, the volume of F_1 V_1 = 643.03 ml. F_2 contained 677.7 mg (0.077 mmol) of *3*. After evacuation of the whole system the connecting cock between F_1 and F_2 was closed and F_1 was filled with CO gas of 581 torr. The CO pressure in the total volume after expansion would be 399.48 torr. After opening the connecting cock a fast pressure drop to 395 torr was observed. After 1 h the pressure was 393 torr and after 20 h 390 torr. The pressure difference of 9.48 torr corresponds to 0.477 mmol of CO or 6.2 mol CO per 1 mol of *3* under normal conditions. To determine if some of the CO gas can be removed, the reaction volume was evacuated and then filled with CO gas under the same conditions as before: there was no pressure drop.

Acknowledgements

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