Synthesis and catalytic activity of carbonyl palladium clusters

Ilya I. Moiseev

N.S.Kurnakov Institute of General and Inorganic Chemistry
USSR Academy of Sciences, Moscow 117907, USSR

Abstract - Palladium carbonyl acetate (PCA), a tetranuclear cluster with a planar nearly rectangular metal skeleton, and related clusters were synthesized. Clusters with planar square or tetrahedral Pd metal cores were prepared by reacting PCA with Na[Mo(CO)₆] or 1,10-phenanthroline (Phen), respectively. Palladium carbonyl hydrides of type [PdPhen(CO)H(OAc)]ₙ, where n = 2 or 4, were synthesized and shown to be catalysts for hydrogenation and oligomerization of alkenes and allenes. Anionic octanuclear cluster Na₂{Pd₄[CO₃(C₅H₄)₃]} containing Pd-Mo bonds provides dehydration of alcohols evidently via a carbene mechanism. Products of decarbonylation of Pd phenantroline carbonyl clusters were shown to be active catalysts for oxidative acetoxylation and alcoxylation of unsaturated hydrocarbons.

INTRODUCTION

Palladium (II) complexes have been known for a long time to be the catalysts for many oxidative reactions (ref.1-3). Up to 1975, when our study was launched some of these reactions have been suggested to be really catalyzed by polynuclear compounds of palladium in oxidative states lower than (+2). In search for such catalytically active compounds or their models we have turned to the methods of metal-carbonyl chemistry as a useful tool for the synthesis of polynuclear compounds. The methods of the synthesis of carbonyl Pd complexes with phosphine ligands are well known now (ref.4-11). However, phosphine, arsine and related ligands are readily oxidized. Bearing in mind the search of materials for oxidative catalysis, we have chosen α,α'-bipyridine (Bipy), 1,10-phenanthroline (Phen), and related hard-oxidizable compounds as stabilizing ligands. Necessary CO ligands were assumed to be removed in either event at the final steps of the synthesis. Our study have resulted in a series of polynuclear Pd compounds including so-called giant Pd clusters (ref.12). In the course of this study we have obtained a number of low-molecular carbonyl palladium clusters. Their chemistry is the subject of the paper.

PALLADIUM CARBONYL ACETATE CHEMISTRY

When solutions of palladium (II) carboxylate Pd(OCOR)₂ (R = Me, Et or Ph) are contacted with CO, reduction of Pd(II) to Pd metal usually occurs. In glacial acetic acid containing alkali metal acetates, reduction of Pd(OAc)₂ with CO results in formation of palladium metal, acetic anhydride, and CO₂ (ref.13):

\[
Pd(OAc)_2 + CO \rightarrow Pd + (OAc)_2 + CO_2
\]  

(1)

In carboxylic acids or (carboxylic acid+benzene) mixtures as solvents, in the absence of alkali metal acetates, we obtained relatively stable complexes of stoichometry RCOO·Pd·CO·nRCOOH where n = 0.5 or 0. Thus, carbonylation (1 atm of CO) of Pd(OAc)₂ in glacial acetic acid at 50°C gave AcO·Pd·CO·0.5AcOH (1). Crystals of 1 lose 0.5 mol of acetic acid per 1 g.-atom of palladium when kept for about 10 days in vacuo over KOH at 20°C, forming palladium carbonyl acetate (PCA) AcO·Pd·00 (2). IR spectra of the complexes show two strong absorption bands in 0-0 stretching region at 1934.
and 1975 cm\(^{-1}\) for 1 and 1940 and 1975 cm\(^{-1}\) for 2 in addition to frequencies corresponding to the bidentate coordinated acetate ligands (ref.13). According to X-ray analysis data, crystals of 1 consist of tetranuclear clusters \(\text{Pd}_4(\text{CO})_4(\text{OAc})_4\) and hydrogen-bonded dimeric molecules of AcOH (Fig.1).

The \(\text{Pd}\) framework of the cluster is nearly rectangular, with almost right angles (83.4° and 96.6°). Acetate-bridged \(\text{Pd}-\text{Pd}\) distances (2.909 Å) are longer, and \(\text{CO}\)-bridged ones (2.663 Å) are shorter than the shortest \(\text{Pd}-\text{Pd}\) distance (2.751 Å) in \(\text{Pd}\) metal (ref.13).

Fig.1. Structure of \(\text{Pd}_4(\text{CO})_4(\text{OAc})_4\cdot2\text{AcOH}\).

The similarities in \(\text{CO}\) and \(\text{COO}\) regions of IR spectra, the chemical compositions and chemical behavior of these complexes and corresponding properties of PCA suggest that all of them contain tetranuclear \(\text{Pd}\) cluster the same as PCA. Therefore, PCA synthesis depicted by eq.2

\[
4 \text{Pd(OAc)}_2 + 8 \text{CO} \rightarrow \text{Pd}_4(\text{CO})_4(\text{OAc})_4 + 2(\text{Ac})_2\text{O} + 4\text{CO}_2
\]

offers a general way to palladium (I) carbonyl carboxylates.

Kinetic study showed that the rates of PCA accumulation at 40°C obey a total second-order equation (ref.14):

\[
w = k_{\text{PCA}}[\text{Pd(II)}][\text{CO}]
\]

In AcOH solutions, in the absence of alkali metal acetate, at 25-40°C palladium (II) acetate is a trimer \(\text{Pd}_3(\text{OAc})_6\) and dissociates slowly. The observed first-order dependence on both \(\text{Pd(II)}\) and \(\text{CO}\) concentrations suggests that \(\text{CO}\) is coordinated with trinuclear palladium (II) acetate at the first stage of the reaction. Reduction of \(\text{Pd(OAc)}_2\) with \(\text{CO}\) was studied also in anhydrous benzene to elucidate possible ways of further reactions of trinuclear carbonyl palladium (II) intermediate complex. Addition of benzene to AcOH solutions was found to give no retardation the PCA formation from \(\text{Pd(OAc)}_2\) and \(\text{CO}\). Volumetric experiments at 60°C showed that benzene solutions of \(\text{Pd(OAc)}_2\) absorb nearly 2 moles of \(\text{CO}\) per 1 g.-atom of \(\text{Pd}\). \(\text{CO}\) appears in gaseous phase along with \(\text{CO}\) absorption though no precipitation of \(\text{Pd}\) metal occurred. After treatment with \(\text{CO}\), a light brown residue was isolated, IR spectrum of which showed a band at 1810 cm\(^{-1}\) ascribed to acyl group bonded to palladium (II) atom. Further evidence for intermediate formation of acyl-palladium (II) complex was provided by trapping of this complex with \(\text{H}_2\text{O}\), ethanol, dihydrogen, and sodium acetate to give acetic acid, ethyl acetate, acetaldehyde, and acetic anhydride, respectively.

The stoichiometric and kinetic data led to conclusion that the reaction of trinuclear carbonyl palladium (II) complex includes \(\text{CO}\) insertion into \(\text{Pd}-\text{OAc}\) bond followed by \(\text{CO}\) elimination resulting in formation of acyl palladium (II) complex \(\text{Pd}_3(\text{COAc})_4(\text{OAc})\text{COCH}_3\).

The coordinated OAc groups in PCA are rather readily replaced by other carboxylic anions by reactions of the corresponding acid with PCA. Thus, PCA was recrystallized from trifluoroacetic acid to give a crystalline complex \(\text{Pd}_4(\text{CO})_4(\text{OCCl})_4\) Complexes \(\text{Pd}_4(\text{CO})_4(\text{OCCl})_4\) and \(\text{Pd}_4(\text{CO})_4(\text{OCCl})_4\) were obtained by recrystallization of PCA from benzene solutions containing \(\text{CCl}_3\text{OOCH}\) and \(\text{CH}_2\text{OClOOCH}\), respectively, see eq. 3.
$\text{Pd}_4(\text{CO})_4(\text{OAc})_4 + \text{RCOOH} \rightarrow \text{Pd}_4(\text{CO})_4(\text{OCOR})_4 + \text{AcOH}$ \hspace{1cm} (3)

$\text{R} = \text{CF}_3, \text{CCl}_3, \text{CH}_2\text{Cl}_2$.  

The similarities in IR spectra, chemical behaviour, and stoichiometry of these compounds with the related data of PCA suggest that all the complexes are analogous to PCA.

The anionic octanuclear cluster $\text{Na}_2[\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4] \cdot 2\text{THF}$ (3) was obtained by reaction of PCA with $\text{Na}[\text{CpMo}(\text{CO})_3]$ in THF (ref.15). X-ray diffraction data showed that the structural unit of the complex 2 contains the centrosymmetric anion $[\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4]^{2-}$ (Fig.2), two sodium cations, and two THF molecules. The cluster 2 has a square planar configuration with Pd-Pd distances 2.675-2.691(2) Å. Each of the Mo atoms is connected with two Pd atoms, Pd-Mo 2.723-2.741(2) Å, all the metal atoms lying in the same plane. Neutral molecular clusters $[\text{Pt}_2\text{M}_4(\text{µ}_2\text{-OR}\text)\text{µ}_2\text{-OR}^\text{3}(\text{µ}_2\text{-C0})\text{µ}_2\text{-C0}]_\text{4}$, where M = Pt, Ni; R = C$_8$H$_8$Me=4, with metal core similar to that of 3 were synthesized recently (ref.16). The three carbonyl ligands attached to each Mo atoms approach Pd, one of them in a triply bridging mode, $\text{µ}_3\text{-CO}$, Pd-O 2.22-2.45(2) Å, and two others are doubly bridging ligands, $\text{µ}_2\text{-CO}$, Pd-C 2.34-2.36 Å. IR spectrum of 3 displays bands at 2000, 1945, 1877, 1830 cm$^{-1}$ corresponding to coordinated CO ligands. The environment of each Mo and Pd atom is similar to that in the known cluster $\text{Pd}_2\text{Mo}_2(\text{µ}_2\text{-CO})_4(\text{µ}_2\text{-CO})_3(\text{µ}_2\text{-C0})_2$ (ref.8). Formation of cluster 3 from PCA is accompanied by displacement of OAc ligands by CpMo(CO)$_3$ anions and by elimination of some carbonyl ligands. Moreover, the reaction is not restricted to ligand substitution processes. Assuming that Mo atoms retain their zero oxidation state as in initial Na[CPMo(CO)$_3$], the observed reaction may be formally described as reduction of Pd($\text{I}$) to Pd($\text{II}$/2), according to eq. 4:

$\text{Pd}_4(\text{CO})_4(\text{OAc})_4 + 6\text{Na}[\text{CpMo}(\text{CO})_3] \rightarrow \text{Na}_2[\text{Pd}_4\text{Mo}_4(\text{µ}_2\text{-C0})_3(\text{µ}_2\text{-CO})_4]^{2-} + [\text{CpMo}(\text{CO})_3]_2 + 4\text{NaOAc} + 4\text{CO}$ \hspace{1cm} (4)

Reaction of PCA with diphenyldiazomethane in benzene solutions resulted in the substitution of CO groups with carbene ligands (ref.17) as described by eq. 5.

$\text{Pd}_4(\text{CO})_4(\text{OAc})_4 + 4\text{Ph}_2\text{CN}_2 \rightarrow \text{Pd}_4(\text{CPh}_2)_4(\text{OAc})_4 + 4\text{CO} + 4\text{N}_2$ \hspace{1cm} (5)

Hydrogenation of diphenylcarbene palladium acetate 4 proceeds through the cleavage of Pd=C bonds yielding diphenylmethane and Pd metal as described by eq. 6.

$\text{Pd}_4(\text{CPh}_2)_4(\text{OAc})_4 + 6\text{H}_2 \rightarrow 4\text{Ph}_2\text{CH}_2 + 4\text{AcOH} + 4\text{Pd}$ \hspace{1cm} (6)

In contrast to hydrogenation of 4, reaction of PCA with $\text{H}_2$ gives no CO hydrogenation products under similar conditions:

$\text{Pd}_4(\text{CO})_4(\text{OAc})_4 + 2\text{H}_2 \rightarrow 4\text{Pd} + 4\text{CO} + 4\text{AcOH}$ \hspace{1cm} (7)

By analogy with CO, free carbene species or carbene donors were expected to reduce Pd($\text{II}$) complexes resulting in Pd carbene complexes similar to PCA. However, our attempt to perform such a reaction with Pd(OAc)$_2$ and Ph$_2$CH$_2$ in
The reaction of PCA with Phen at a ratio Phen: Pd = 1:1 in AcOH solutions in Ar atmosphere, complex \( \text{Pd}_4(\text{CO})_2\text{Phen}_4(\text{OAc})_4 \), was prepared in accord with eq. 13 (ref. 21).
Carbonyl palladium clusters

\[
\text{Pd}_4(\text{CO})_4(\text{OAc})_4 + 4 \text{ Phen} \longrightarrow \text{Pd}_4(\text{CO})_2\text{Phen}_4(\text{OAc})_4 + 2 \text{ CO}
\]  
(13)

IR spectrum of 6 shows a strong band at 1800 cm\(^{-1}\) corresponding to the bridging CO group stretching mode. X-ray analysis data showed that 6 contained a nearly tetrahedral cluster of palladium atoms (Fig. 4).

The next CO ligand was supposed to be eliminated from the cationic intermediate to form complex di-cation 7:

\[
\text{PhenCd(CO)PdPhen}_2^+ \longrightarrow \text{PhenCd(CO)PdPhen}_2^+ + \text{ CO}
\]  
(15)

Tetrahedral cluster 6 is conceivably formed by dimerization of coordinatively unsaturated species 7. The shortest distance between the axes of PhenCd(CO)PdPhen groups in cluster 6 (see Fig. 4) was found to be equal to ca. 1.8 Å (ref. 21). At this distance, overlapping between the two PhenCd(CO)PdPhen group orbitals might be effective enough to contribute into the core stabilization of cluster 6. By treating with CO solutions of PhenCd(CO)_2 and Phen (PdPhen = 1:1) in \(\text{AcOH}\) at 20°C complex PhenCd(CO)PdPhen^2+ (8) characterized by elemental analysis data, molecular weight and IR spectrum was obtained, as shown by eq. 16.

\[
4 \text{ Pd(OAc)}_2 + 4 \text{ Phen} + 4 \text{ CO} \longrightarrow \text{Pd}_4(\text{CO})_4\text{Phen}_4(\text{OAc})_4 + 4 \text{ CO}_2
\]  
(16)

In a tetrahedron, six edges are available which could be occupied by CO ligands. In fact, along with the complex 8 some higher carbonyl complexes are seemingly formed as by-products of carbonylation of Pd(OAc)_2 under the conditions of reaction 10. Another side reaction might be a reductive carbonylation resulting in carbonyl hydrides. Thus, a complex of a tentative composition \[\text{PdPhen(CO)H(OAc)}\]\(_n\) was obtained by carbonylation of complex 8 in AcOH solution at 50°C. IR and \(^1\)H NMR spectra show a band at 1700 cm\(^{-1}\) (bridging CO group) and a singlet at \(-15.3\) ppm (H atom in a bridging position), respectively. Molecular weight of the compound in ethanol solution was found to correspond to \(n = 4\) (M.W.

\[
\text{PdPhen(CO)H(OAc)}_4 \text{ is equal to 1496). This value seems to be a lower limit of the molecular weight since conductivity of the complex in ethanol and}
\]
other polar solvents corresponds to one of a weak electrolyte. Nevertheless, the data suggest the complex may be formulated as $\text{Pd}_4\text{Phen}_4(\text{CO})_4(\text{OAc})_4$ (2), its formation being depicted as follows:

$$\text{Pd}_4\text{Phen}_4(\text{CO})_4(\text{OAc})_4 + 2 \text{CO} + 4 \text{AcOH} \rightarrow \text{Pd}_4\text{Phen}_4(\text{CO})_4\text{H}_4(\text{OAc})_4 + 2 \text{CO}_2 + \text{Ac}_2\text{O}$$ (17)

The amounts of CO consumed and CO formed are in accord with eq.11. Another way to complex 9 could be hydrogenation of complex 8. At the exposition of solutions of 8 in AcOH under H$_2$ at 20-50°C, 2 moles of H$_2$ per mole of complex 8 were absorbed. IR and $^1$H NMR spectra of the complex obtained reveal a band at 1790 cm$^{-1}$ and singlet at -15.3 ppm, respectively, coinciding with that of complex 2. However, the molecular weight data correspond to n = 2 in the above formula (M.W. found 800, M.W. calc. for $[\text{Pd Phen(\text{CO})H(OAc)}]$ is equal to 749). Therefore, this complex may be formulated as $\text{Pd}_2\text{Phen}_2(\text{CO})_2\text{H}_2\cdot(\text{OAc})_2$ (10).

Complexes related to 9 and 10 were prepared by hydrogenation of AcOH solutions containing $\text{Pd}(\text{OAc})_2$ and Phen (Phen:Pd ratio 1:1) and following carbonylation of the solution (ref.22). The product of hydrogenation was found to be a polynuclear hydride complex of composition $[\text{Pd}_2\text{Phen}_2\text{H}(\text{OAc})_2]_n$ (11) where n = 100 (ref.23). A carbonyl hydride substance, possibly a mixture of complexes, of average composition $\text{Pd}_2\text{Phen}_2(\text{CO})_2\text{H}_2\cdot(\text{OAc})_2$, (12) was obtained by carbonylation of complex 11. $^1$H NMR and $^3$IR spectra of complex 12 are similar to those for complexes 9 and 10.

**CATALYTIC REACTIONS**

PCA has been shown to be an intermediate compound in the reductive carbonylation of $\text{Pd}(\text{OAc})_2$ in AcOH solutions containing NaOAc, as a result AcO$_2$ and Pd metal were formed (see eq.1). This reaction being combined with reoxidation step

$$\text{Pd} + \text{Ox} + 2 \text{AcOH} \rightarrow \text{Pd}(\text{OAc})_2 + \text{Red}$$ (18)

($\text{Ox}$ is an oxidant, $\text{Red}$ is a reduced form of the Ox) could be used to produce carboxylic acid anhydride under mild conditions as depicted by eq.18.

$$\text{AcOH} + \text{CO} + \text{Ox} \rightarrow (\text{Ac}_2\text{O})_2 + \text{CO}_2 + \text{Red}$$ (19)

Dehydration of AcOH is usually performed at high temperatures (500-600°C) because of thermodynamic restrictions:

$$2 \text{AcOH} \rightarrow (\text{Ac}_2\text{O})_2 + \text{H}_2\text{O}, \quad \Delta G^{0} = +12 \text{ kcal/mole}$$ (20)

Reaction (12) inherently includes oxidation of carbon monoxide (eq.14):

$$\text{CO} + \text{Ox} \rightarrow \text{CO}_2 + \text{Red}$$ (21)

as a complementary exoenergetic reaction. In the case of $\text{Ox} = \text{O}_2$ and $\text{Red} = \text{H}_2\text{O}$, the thermodynamics of reaction 21 is characterized by $\Delta G^{0} = -61$ kcal/mole. So overall process 18, as a sum of reactions 20 and 21, is characterized by $\Delta G^{0} = -49$ kcal/mole permitting the reaction at room temperature. However, in the case of $\text{Ox} = \text{O}_2$, water should be removed from reaction mixture effectively because CO oxidation

$$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$$

dominates in AcOH-water solution.

PCA was found to be inert towards alkenes and was decomposed in H$_2$ atmosphere. Acetylene is polymerized in AcOH solutions of PCA and converts into vinylaceta te with a small yield. No oxidation of alkenes or arenes was observed in the presence of PCA in AcOH or alcohol solutions. However, addition of Phen to PCA solution results in formation of an active catalyst arising from PCA decarbonylation by the action of Phen and O$_2$ (see eq. 9,11, 12). Thus, propylene and 2-methylpropene were oxidized at 20°C and 1 atm in methanol solutions which initially contained Phen and PCA at a ratio Phen: Pd = 1:1. Selective formation of allylmethyl and methallylmethyl ethers was observed under these conditions (ref.24).
The catalyst of this reaction seems to be a complex of type \( \text{Pd}_2\text{Phen}_2(0\text{Ac})_x \) (see eq.12). In contrast with this complex, palladium (II) compounds are known to provide catalytic oxidation of alkenes and alcohols into acetals and ketals (ref.2). The same complex was found to be a catalyst for oxidative acetoxylation of alkylarenes (ref.25) and alkenes (ref.26). It is noteworthy that alkylarenes undergo oxidative substitution into aromatic ring in the presence of Pd (II) compounds instead of side-chain substitution. In the presence of Pd (II) complexes alkenes are mainly converted into vinyl esters (refs.22-24), the main products being the main compounds containing more than 1% of water. In contrary to that, no water influence was observed in the presence of \( \text{Pd}_2\text{Phen}_2(0\text{Ac})_x \).

Contrary to expectations, complexes 2 and 10 do not catalyze isomerisation of 1-alkenes in spite of the presence of coordinated hydrogen. Both IR band at 1790 cm\(^{-1}\) and singlet at -15.3 ppm in \(^1H\) NMR spectrum disappeared after addition of unsaturated compounds to the solutions of the complexes in AcOH or alcohols. Saturation of the solution with ethylene gives rise to ethyl acetate, propionic aldehyde, and diethyl ketone in amounts commensurable with those of the complex used. The reaction may be pictured as the insertion of alkene molecule into Pd-H bond followed by carbonylation of the Pd-alkyl bond formed. The Pd-\(\text{COC}_2\text{H}_4\) fragment arises seemingly undergoing insertion of the second \(\text{C}_2\text{H}_4\) molecule and/or hydrogencyclisation by the coordinated hydrogen to give rise to diethyl ketone and propionic aldehyde, correspondingly. The final Pd compounds, which contain \(\text{C}_2\text{H}_4\) and Phen molecules as stabilizing ligands, were found to be active in oligomerisation of ethylene into butenes and hexenes. The complexes provide also catalytic hydrogenation of alkenes and alkynes under H\(_2\) atmosphere at 25-50°C. The reaction is neither fast nor selective. Thus, hydrogenation of phenylacetylene at 50°C and 1 atm of H\(_2\) in the presence of 2 or 10 as the starting compounds for catalyst formation was found to give styrene in 35-50% yield and ethylbenzene, 10-20%, after 24 h. No hydroformylation nor alkoxycarboxylation occurred in the presence of Pd phenanthroline carbonyl hydrides.

\(\text{Pd}_2\text{Mo}\)-cluster 3 was found to be a catalyst for alcohol oxidation. Thus, methanol is converted into methyl formate, oxidation of ethanole gives rise to diethyl acetal, and that of benzyl alcohol results in benzaldehyde formation at 60-80°C and 1 atm of O\(_2\). The starting complex was destroyed under reaction conditions and the observed catalytical activity was due to the products of oxidation of the starting cluster 3. Dehydration of alcohols in the presence of \(\text{Pd}_2\text{Mo}\)-cluster was found to proceed at 60-80°C under Ar atmosphere or in vacuo (ref.27). No ethers were found in the reaction mixture. In the case of methanol and ethanol the main product of dehydration is white wax-like substance, trans-Stilbene was obtained by dehydration of benzyl alcohol. Dehydration of alcohols under essentially non-acidic conditions is rather unexpected. No less unusual feature of the reaction is the dehydration of methanol and benzyl alcohol under mild conditions, despite of the absence of H-atom at \(\alpha\)-position to hydroxyl groups in their molecules. All the facts mentioned suggest to involve carbene species in the reaction. The step of the reaction appears to be oxidative addition of alcohol molecule to Mo-Pd bond. The complex containing both Mo-coordinated hydroxyl anion and Pd-5-bonded alkyl group is formed at this step. Proton transfer from the alkyl group to the coordinated hydroxyl results in formation of complex containing coordinated water molecule and carbene ligand, which gives rise to organic products. In the course of the reaction the starting complex may be partially decarbonylated, so it is unclear whether the reaction is catalyzed by cluster 2 or by products of its transformations. It is doubtless that the presence of Pd-Mo bond in the catalyst is necessary. Neither FCA nor \(\text{Na}[\text{Mo}=\text{CO}_3]\) are active in the reaction under consideration.

It is obviously that hydrogenolysis of the intermediates containing coordinated alkyl group or carbene ligand would lead to corresponding alkanes. Our attempts to carry out hydrogenation of benzyl alcohol in the presence of \(\text{Pd}_2\text{Mo}\)-cluster failed, however, because of instability of the complex under H\(_2\). Nevertheless, toluene in amount commensurable with that of cluster 2 was found by H\(_2\) treatment of the solution of 3 in benzyl alcohol after preliminary exposition under Ar for 30-40 days at 80°C.

Acknowledgements  The author is deeply indebted to Professor M.N.Vargaf-tik, Drs T.A.Stromanova, I.P.Stolarov, I.N.Busygina, E.V.Evdokimova for enthusiastic collaboration. I am especially indebted to Professor M.A.Porai-Koshits, Professor Yu.T.Struchkov, Drs L.G.Kuz'mina, A.S.Antayshkina,
T.S. Khodashova, and S.B. Katzer for carrying out X-ray diffraction studies and for many helpful discussions.

REFERENCES