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Gold-containing derivatives of cyclopropanecarboxylic acid amides

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Abstract

The interaction of substituted cyclopropanecarboxylic acid amides with $[(Ph_3PAu)_3O]BF_4$ (I) has been studied. The reaction of I with cyclopropanecarboxylic acid *p*-nitroanilide leads to the gold derivative with the Au–N bond, the small cycle being unaltered. The interactions between lithiated cyclopropanecarboxylic acid *N*,*N*-diethylamides and I afford the organogold derivatives of the amides with gold bonded to the carbon of the small cycle. The compounds obtained were characterized by IR, ^{1}H and ^{13}C NMR spectral data. An X-ray structural study of [triphenylphosphinegold(*p*-nitrophenyl)carbamoyl] cyclopropane and 1-triphenylphosphinegold-1-diethylcarbamoylcyclopropane was carried out.

The interaction of lithiated derivatives of cyclopropanecarboxylic acid amides, in excess, with I gives unexpectedly stable anionic complexes of gold(I), (e.g. 1-diethylcarbamoylcyclopropyl)aurate. The potassium salt $[(\overline{\mathrm{CH_2CH_2C}})\mathrm{CONET_2}]_2\mathrm{AuK}$ is stable in air, and it was isolated after treatment of the lithium salt of bis(diethylcarbamoylcyclopropyl)aurate with potassium carbonate. Its dimeric nature was confirmed by an RDF study, the Au_2K_2 fragment being a distorted tetrahedron.

Introduction

A great number of monovalent gold compounds of the type RAuL with various organic substituents including some containing functional groups has been reported [1]. However, cyclopropylgold derivatives have only recently been described.

Separate consideration of the cyclopropyl derivatives is not a coincidence. It is because of the unique properties of the cyclopropyl system originating from its electronic structure. One can mention, for example, the conjugation of the small cycle with different unsaturated groups, a transfer of effects through the three-membered cycle, and an ability to stabilize cationic centers [2].

The chemistry of organogold compounds also has some peculiarities. There is a similarity in the behaviour of gold and mercury compounds, on the one hand, but on the other hand gold as a post-transition element has a tendency to form polynuclear complexes.

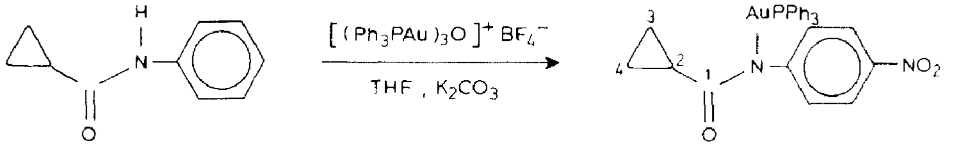
Thus, cyclopropyl gold derivatives are of evident interest arising from peculiarities of the cyclopropyl system and the post-transition character of gold.

We have evaluated previously methods of synthesis of systems containing both the small cycle and the gold atom. We obtained two types of cyclopropyl gold derivatives: with an Au–C bond in the side-chain of a cyclopropane compound and with gold bound to carbon in the small cycle [3,4]. To obtain compounds of the first type we used the reaction previously described [5]. It involves the auration of organic compounds by tris(triphenylphosphinegold)oxonium tetrafluoroborate. A series of substituted acetylcyclopropanes was used as starting materials [3]. To obtain compounds of the second type having the metal bound to carbon in the small cycle we developed a procedure involving metallation of the starting cyclopropane by lithium diisopropyl amide (LDA) and subsequent interaction with a halogold complex or the gold oxonium salt. The latter reaction was also used by us for auration of dicyclopropyl ketone and the product of its aldol condensation [4].

Continuing our previous efforts, we have studied in this work the interaction between cyclopropanecarboxylic acid amides or their lithiated derivatives and gold-containing complexes. We obtained compounds of two structural types, namely with gold–nitrogen and gold–carbon bonds.

Results and discussion

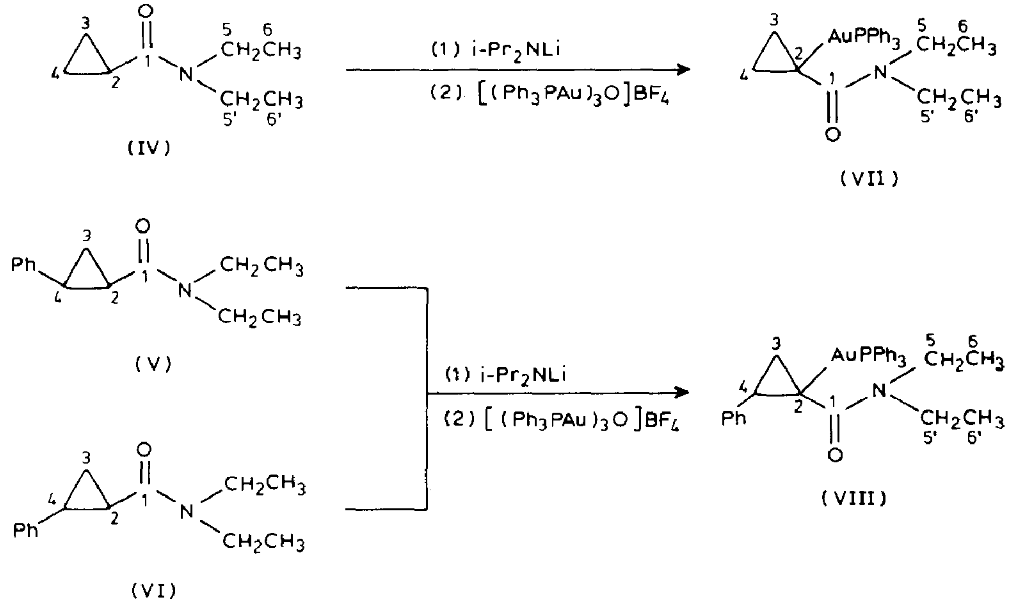
We have previously reported the procedure for synthesis of *N*-aurated aliphatic and aromatic acid amides by reacting them with tris(triphenylphosphinegold)oxonium tetrafluoroborate (I) in the presence of potassium carbonate [6]. We extended the method to amides of the cyclopropane family and performed the reaction with cyclopropanecarboxylic acid *p*-nitroanilide (II). We have found that the interaction of the latter with I in the presence of potassium carbonate leads to complex III where the hydrogen is replaced by the AuPPh$_3$ group. As in the auration of methyl cyclopropyl ketones [3], the three-membered cycle is unaltered in the new complex.



(II) (III)

The structure of III is confirmed by IR, ^{1}H and ^{13}C NMR spectral data.

To prepare the compounds with gold in the small cycle we used the procedure involving the metallation of *N*,*N*-disubstituted cyclopropanecarboxylic acid amides by LDA occurring at the α-carbon and subsequent interaction of the lithiated derivative with [(Ph$_3$PAu)$_3$O]BF$_4$ (I). As the starting materials we chose diethylamides of cyclopropanecarboxylic (IV), *cis*- and *trans*-2-phenylcyclopropanecarbo-



xylic acids (V and VI) and obtained α-aurated at the cyclopropane ring amides VII and VIII *.

The absorption bands of the carbonyl groups of compounds VII and VIII are shifted by 40 cm^{-1} in the IR spectra to lower frequencies compared with starting amides IV–VI. Similar shifts were observed previously for α-aurated ketones of the cyclopropane family [3,4].

^{1}H and ^{13}C NMR spectra of compound VII correspond to the structure shown. One can notice the nonequivalence of the CH_2 groups of the diethylcarbamoyl substituent (see below).

Contrary to auration of methyl cyclopropyl ketones [3], the formation of organogold derivatives of 2-phenyl substituted cyclopropanecarboxylic acid amides is accompanied by *cis–trans* isomerization. In the former case the configuration of the starting ketones does not change. Despite the stereochemical structure of the starting amide (V and VI), the reaction product is a mixture of *cis* and *trans* isomers of VII. The ^{13}C NMR spectra of the organogold complexes obtained from *cis* and *trans* isomers (V and VI) are identical, all resonances in the spectra being doubled (see Table 1).

The isomerization is probably due to the fact that the reaction involves the cyclopropyl carbanion (IX or XI). The isomerization of these carbanions is facilitated by the electron-withdrawing substituent present which can stabilize the planar intermediate X. Unsubstituted or alkyl substituted cyclopropyl carbanions in which such a stabilization is impossible are known to react with retention of configuration [8,9].

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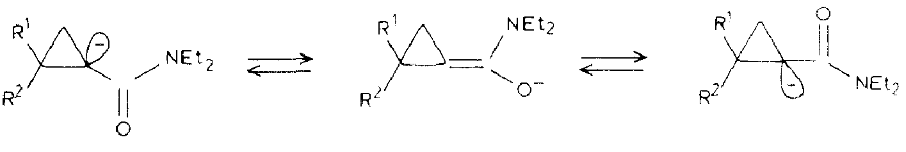
* Direct auration of amides IV–VI by tris(triphenylphosphinegold)oxonium does not occur in the presence of K_2CO_3.



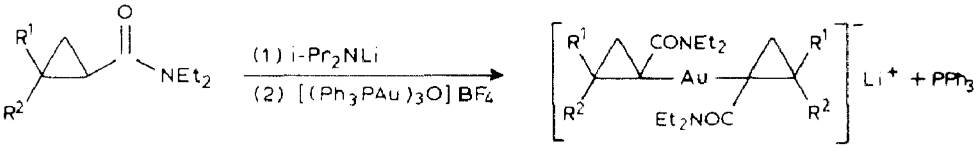
(IX) (X) (XI)

(R^1 = H, R^2 = Ph ; R^1 = Ph, R^2 = H)

We could not separate *cis* and *trans* isomers of VIII since they have similar physico-chemical properties.

One of the isomers of VIII predominates, but, unfortunately, its nature could not be identified. The signal in ^{13}C NMR spectrum for carbon of the three-membered ring which has no substituents is not as informative as has been observed previously in the case of 2-phenyl substituted acetylcyclopropanes [3]. We believe that the gold complex from *cis*-2-phenylcyclopropanecarboxylic acid diethylamide VIII dominates. The resonance for the carbonyl carbon of the starting diethylamide V is observed in a higher field compared with the *trans*-isomer (167.1 and 170.7 ppm, respectively). The resonances for carbonyl carbons in ^{13}C NMR spectra of the mixture VIII observed at 175.82 and 178.16 ppm are characterized by approximately the same difference in the shifts, the integral intensity of the high-field signal being twice the down-field one.

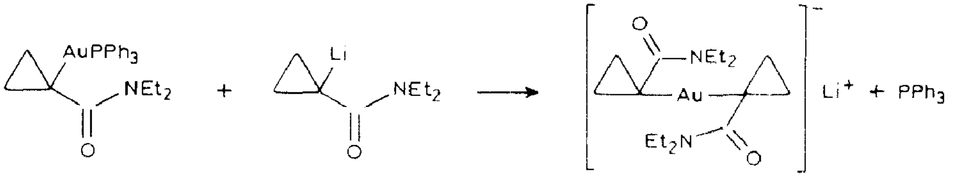
When lithiated cyclopropanecarboxylic acid amides in excess react with I (assuming that all three $AuPPh_3$ groups take part in the reaction), the reaction affords, together with the triphenylphosphine complexes (VII or VIII) the stable salts of anionic gold(I) complexes XII or XIII. Highest yields of the aurates are achieved when a four-fold excess of the lithium derivative is used. The stereochemistry of the aurate formation was not studied.



(IV : R^1 = R^2 = H ,
V : R^1 = H , R^2 = Ph ;
VI : R^1 = Ph , R^2 = H)

(XII : R^1 = R^2 = H (83%) ;
XIII : R^1 = H , R^2 = Ph (49%))

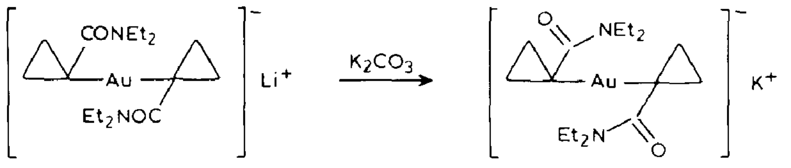
The anionic complexes can be also obtained starting from the organogold compound adding it to the reaction mixture with an excess of the corresponding lithium derivative. Triphenylphosphine thus leaves the coordination sphere of gold and is substituted by the corresponding carbanion.



(VII) (XII)

Dicyclopropylaurates, preparation of which is reported in the present work, are of unique stability. Their properties differ markedly from those of dialkylaurates and are more close to those of diarylaurates. In particular, lithium salts of XII and XIII can be kept in the air for several days.

We have transformed lithium salt XII into potassium salt XIV by treating the former with potassium carbonate.



(XII) (XIV)

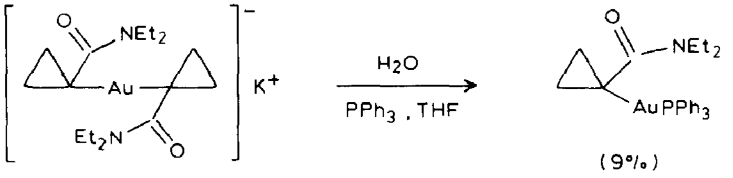
Aurate XIII with a phenyl group also exchanges Li^+ for K^+ under the action of K_2CO_3, but solubility of both the salts is similar preventing their separation. To this end, we carried out the substitution of a cation in aurate for other metal. Other workers failed to do this previously [10].

Potassium salt XIV is a white powdered solid, insoluble in organic solvents, and stable in the air for a long period of time.

The stretching frequency of the carbonyl group in XIV is shifted to lower frequencies in the IR spectrum (1545 cm^{-1}). In the ^1H NMR spectrum there are resonances from protons of the small cycle and ethyl groups of the diethylcarbamoyl fragment (multiplet at 0.87–1.47 ppm and two quadruplets at 3.30 and 3.98 ppm with the coupling constant *J* 7 Hz). In the ^{13}C NMR spectrum (see Table 1) one can see the signals for carbons of the small cycle (10.40 ppm, two carbons of the CH_2-groups and 29.87 ppm, carbon bonded to gold) and for ethyl groups (13.13 and 12.02 ppm, CH_3 carbons, 40.63 and 37.97, CH_2 carbons).

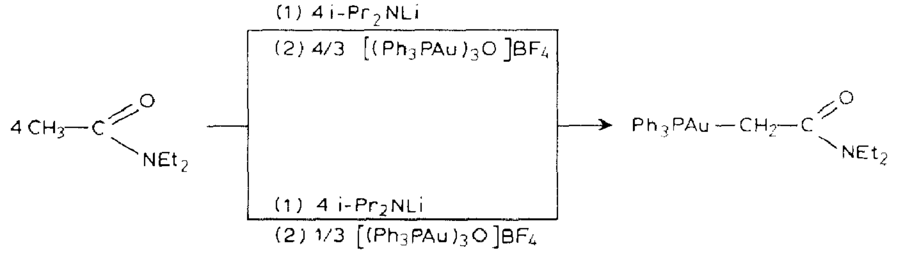
Lithium salt XII is a crystalline material. There is a broad band near 3400 cm^{-1} ascribed to the OH group in its IR spectrum. In addition to the signals of the potassium salt XIV, mentioned above, the ^1H NMR spectrum of XII has a singlet from OH protons at 4.83 ppm. There are probably water molecules in the crystal lattice of the compound. This inclusion can arise from the smaller size of the lithium atom compared with the potassium atom. It is likely that the water molecules damage compound XII from "inside", thus lowering its stability. Lithium salt XII is more soluble than the potassium one, but in water it dissolves with decomposition.

We have investigated the interaction of aurate XIV with water and hydrogen chloride. Water decomposes XIV, but the stability of the salt with respect to hydrolysis increases in the presence of PPh_3. Mixing of XIV with water for many hours in the presence of PPh_3 produces triphenylphosphine complex VII in a low yield (9%).



One can increase the yield of the triphenylphosphine complex (up to 33%) in the reaction of aurate XIV with water using pyridine as a highly coordinating solvent, but in this case half of the starting aurate is recovered unreacted.

Interaction of XIV with equimolar amounts of 0.1 *N* hydrogen chloride in the presence of triphenylphosphine produces, in a few minutes, the neutral triphenylphosphine complex VII.



Therefore, chemical behaviour of dicyclopropylaurate salts differ considerably from those of known dialkylaurate. Their properties are closer to those of diarylaurates.

To demonstrate that the isolation of stable lithium and potassium salts of cyclopropanecarboxylic acid amides arises the nature of the cyclopropane fragment of the molecule, we have studied the reaction of the lithium derivative of *N*,*N*-diethylacetamide with [(Ph$_3$PAu)$_3$O]BF$_4$. It appeared that independently of the reagent ratio *N*,*N*-diethylacetamide gives only one product, namely α-aurated amide XV.

The crystal and molecular structures of the compounds with N–Au and Au–C bonds, namely of [triphenylphosphinegold(*p*-nitrophenyl)carbamoyl]cyclopropane (III) and 1-triphenylphosphine-1-diethylcarbamoylcyclopropane (VII), were evaluated on the basis of an X-ray structural investigation.

The structure of III and bond lengths are presented in Fig. 1. The gold atom is bound to the amide nitrogen and phosphorus of PPh$_3$. The Au–N bond length is 2.039(5) Å, and it is practically the same distance as in *N*-aurated *p*-nitroacetanilide [6]. The Au–P bond length (2.234 Å) also falls in the range of typical distances in gold complexes with triphenylphosphine [11–13].

The intramolecular bond angle NAuP (174.7(2)°) differs from the ideal value of 180°, but related deviations from linearity in gold complexes are common and may arise from effects of the crystal field.

The carbonyl group is projected on the disector of the angle C(3)C(2)C(4) of cyclopropane (the torsion angles C(9)C(2)C(1)O(1) and C(4)C(2)C(1)O(1) are 32.6 and 34.3°, respectively). This mutual arrangement of the carbonyl and cyclopropyl groups is the most favourable in energy and provides the overlapping of the π^* orbitals of the C=O group and the cyclopropane banana bond system. As a result, the C(3)–C(4) bond distance of the small cycle decreases to 1.45(2) Å and becomes noticeably less than that in unsubstituted cyclopropane (1.5096(15) Å) [14]. The shortening of the C(1)–C(2) bond (1.233(9) Å) compared with that in *N*-aurated *p*-nitroacetanilide (1.52(1) Å [6]), as well as the lengthening of the C–O bond (1.233(7) Å) compared with the common value of 1.19–1.20 Å also indicates the conjugation of the cyclopropyl system with the carbonyl group. These structural findings clearly show that in this case the cyclopropyl derivative has a tendency to display some "olefinic" properties.

The carbonyl group is also conjugated with an unshared nitrogen electron pair (O(1)C(1)C(2)N(1) and C(1)N(1)C(5)Au fragments are almost coplanar, with the corresponding angle being 6°). The configuration of nitrogen atom is trigonal-planar.

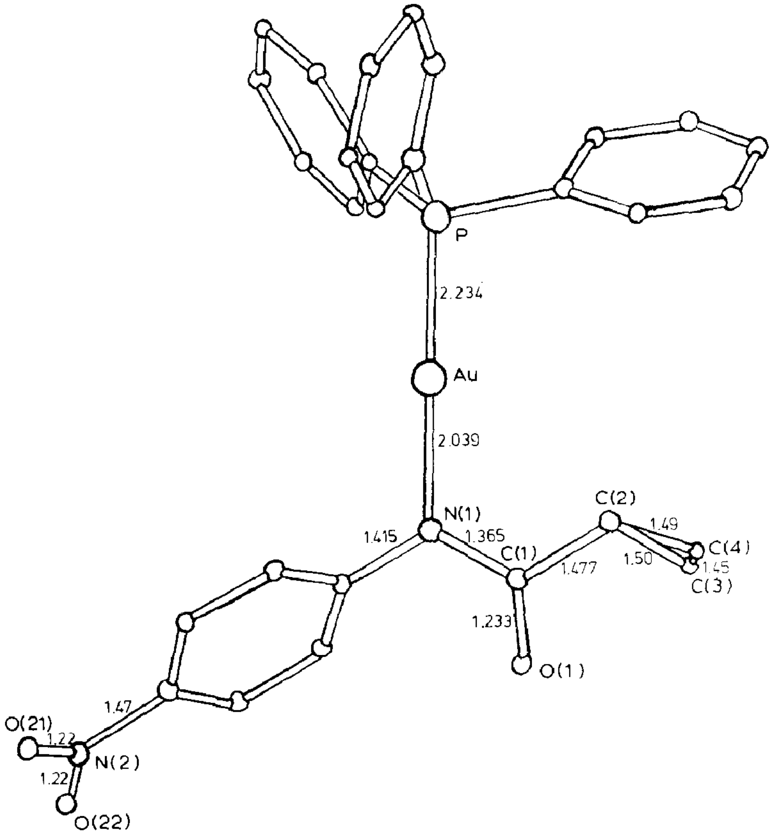


Fig. 1. Molecular structure of [triphenylphosphinegold(*p*-nitrophenyl)carbamoyl]cyclopropane (III).

The *p*-nitrophenyl ring, however, is out of the general system of conjugation, since the dihedral angle between the phenyl plane and the C(1)N(1)C(5)Au plane is 56.5 °.

The gold atom has a transoid orientation with respect to the carbonyl group ruling out the possibility of additional intramolecular coordination of the type Au... O. In this molecule, as in (α-triphenylphosphinegoldcyclopropyl) cyclopropyl ketone [4], the distance between Au and H at C(2) of the three-membered ring is shortened and equal to 2.58 Å. Such interactions have previously been observed in electron deficient transition metal complexes [15].

The structure and bond distances of 1-triphenylphosphinegold-1-diethylcarbamoylcyclopropane (VII) are shown in Fig. 2.

The gold atom forms practically colinear (the angle is 178.2(2)°) bonds with the C(2) atom of cyclopropane and the P atom of PPh_3. The Au–P (2.281(2) Å) and Au–C(2) (2.045(8) Å) bond lengths are quite usual [11–13].

Contrary to what is observed in aurated dicyclopropyl ketone [4] and cyclopropane carboxylic acid *p*-nitroanilide III, the orientation of the carbonyl group in VII is such that its conjugation with the small cycle is minor (the C(3)C(2)C(1)O torsion angle is equal to 37°, while that of C(4)C(2)C(1)O is 103°). The reason is probably sterical, since the bulky ethyl groups do not allow the C=O group to adopt favourable conformation for conjugation with the small cycle. Nonequivalence of the diethylcarbamoyl CH_2 groups (see above) agrees with such an explanation.

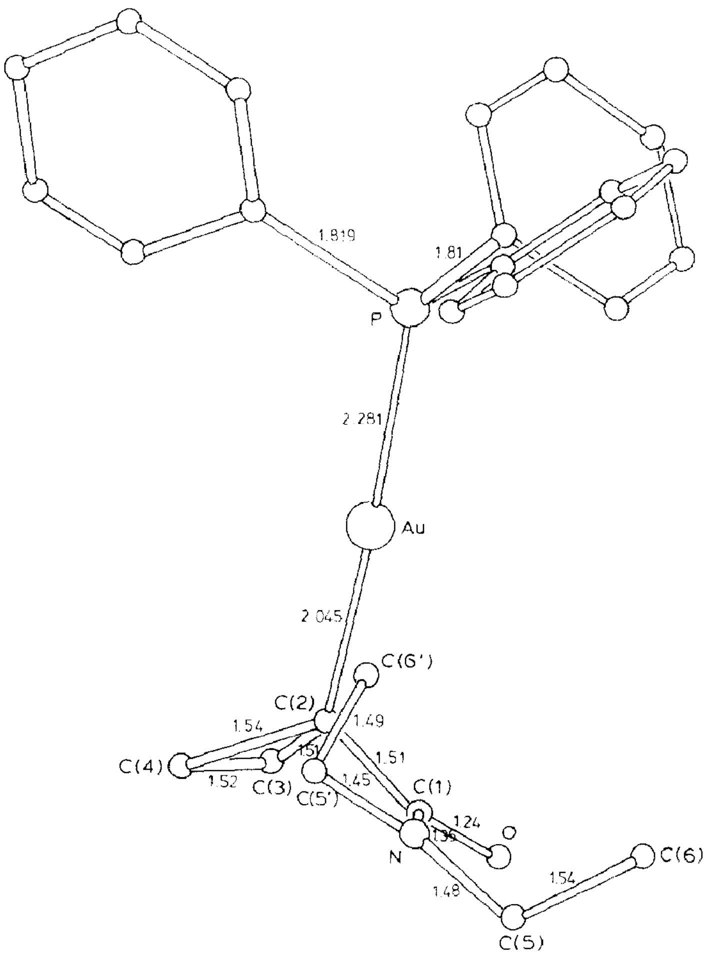


Fig. 2. Molecular structure of 1-triphenylphosphinegold-1-diethylcarbamoylcyclopropane (VII).

The N atom has the trigonal-planar configuration (the sum of bond angles is equal to 359.8°). The N–C(1) bond length (1.35(1) Å) is significantly shorter compared with usual values of single bonds (1.45 Å), longer than double ones (1.27 Å), and accurately corresponds to the one-and-a-half bond (1.34 Å) [16]. The C(1)–O bond distance (1.24 Å) is somewhat longer than the common value of 1.19–1.20 Å [17]. This geometry of the O–C(1)–N fragment indicates the conjugation of a nitrogen unshared electron pair with the carbonyl group, typical of amide fragments.

All other parameters of the molecule are typical and do not require a detailed discussion.

The potassium salt of bis(1-diethylcarbamoylcyclopropyl)aurate (XIV) has been studied by an X-ray crystallography using the method of radial distribution functions (RDF) [18]. This revealed the dimeric nature of the salt shown in Fig. 3.

The gold–gold and gold–potassium bond distances are 3.60 and 3.12 Å, respectively. The fragment K–Au–K–Au is a distorted tetrahedron. The three-membered cycles form bridges between Au and K atoms indicating that the carbon atom forms a three-center, two-electron type of C–Au bonding. The Au–C bond direction of the

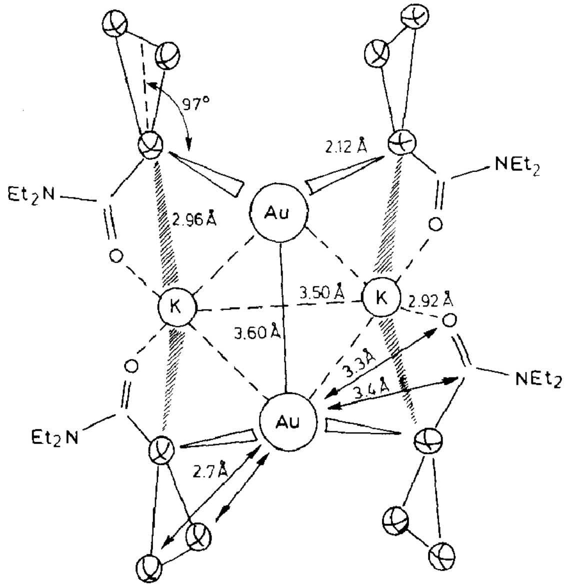


Fig. 3. Molecular structure of the potassium salt of bis(1-diethylcarbamoylcyclopropyl)aurate (XIV).

small ring carbon having a common tetrahedral configuration is shown with an arrow in the scheme and is located approximately halfway between the directions C–K and C–Au. The Au–C and C–K distances are equal to 2.12 and 2.96 Å, respectively. The distances between gold and carbons of CH_2 groups of small cycles are rather short (2.7 Å). In other words, there is a strong inclination of the cyclopropane ring towards gold, the angle between the small ring plane and the C–Au bond being 97°. This fact supports the hypothesis of three-center, two-electron bonding of the metal and the carbons of the small ring (for comparison: in unsubstituted cyclopropane the angle between the small ring plane and the C–H bond is equal to 122° [19]).

One of the heteroatoms of the diethylcarbamoyl substituents (N or O) has a rigid orientation relative to the potassium atom. The distance between potassium and the heteroatom is 2.92 Å. The RDF technique does not allow us to say unambiguously what particular atom, N or O, is coordinated to the potassium atom. We believe that the coordination of K with O is more probable.

In conclusion, the data obtained suggest that the structure of the potassium salt of bis(1-diethylcarbamoylcyclopropyl)aurate XIV resembles that of diarylaurates. The main difference between the structure of XIV and that of lithium bis(dimethylaminomethylphenyl)aurate (XVI) is in the geometry of the fragments Au_2K_2 and Au_2Li_2. The former is a distorted tetrahedron, while the latter is square-planar [20]. The difference is possibly because of the electron configuration of the bridging carbon of the small cycle which is bound with both the metals and the diethylcarbamoyl moiety coordinated to potassium atom. Besides, there is a more pronounced tendency to formation of the two-electron, two-center C–Au bond in the lithium salt of bis(dimethylaminomethylphenyl)aurate [20]. It is also possible that the stability of XIV arises from geometry of potassium atom providing its successful incorporation into the dimeric molecule.

Experimental

IR spectra were registered on a IKS-29 spectrophotometer in Nujol mulls. ^1H NMR spectra were recorded on a Varian T-60 instrument (60 MHz) using tetramethylsilane as internal standard. ^{13}C NMR spectra were obtained on a CFT-20, FT-80 instrument (20 MHz).

The details of an X-ray experiment, calculation of the radial distribution functions and their interpretation are given elsewhere [18].

Cyclopropanecarboxylic acid p-nitroanilide (II)

The mixture of 4.80 g (0.035 mol) of *p*-nitroanilide and 5.49 ml (5.24 g, 0.044 mol) of dimethylaniline was heated up to 35 °C and cyclopropanecarboxylic acid chloroanhydride (4.0 g, 0.038 mol) was slowly added with intense stirring. After stirring for 30 min, the reaction mixture was poured into 50 ml of a 2% solution of hydrogen chloride. The precipitate formed was washed with 2% hydrogen chloride (3 × 30 ml) and recrystallized from ethanol to produce 3.0 g (38%) of II, m.p. 179–180 °C.

Found: C, 58.08; H, 5.24; N, 13.57. $C_{10}H_{10}N_2O_3$ calcd.: C, 58.25; H, 4.89; N, 13.57%. IR (cm^{-1}): 3300m, 3230m, 3120m, 1680m, 1635s, 1565s, 1515s, 1420s, 1350s, 1310s, 1270s, 1210s, 1185s, 1120m, 1077w, 1049w, 960s, 832w, 821w, 756s, 730m, 698w, 687w, 650w, 530w, 500m.

[Triphenylphosphinegold(p-nitrophenyl)carbamoyl]cyclopropane (III)

To a solution of II (0.43 g, 2,1 mmol) in 40 ml of absolute THF, 0.10 g of potassium carbonate and 1 ml of water were added. I (1.0 g, 0.67 mmol) was added after 5 min to the reaction mixture and the latter was stirred for 1.5–2 h to achieve complete dissolution of the oxonium salt. The solution turned yellow. Potassium carbonate was then added to remove water, the solution filtered, and the filtrate evaporated in vacuo. The residual light-yellow powder was dissolved in chloroform, filtered, and diluted with ether. Light-yellow crystals of III (1.0 g, 75%) were isolated, m.p. 205–207 °C with decomposition.

Found: C, 50.53; H, 3.40; N, 4.29; Au, 29.91. $C_{28}H_{24}N_2O_3AuP$ calcd.: C, 50.61; H, 3.64; N, 4.21; Au, 29.65%. IR (cm^{-1}): 1612s, 1578m, 1504s, 1345s, 1290s, 1210m, 1111m, 1000w, 925w, 862w, 850w, 827w, 759m, 700s, 550s, 518m, 501m.

^1H NMR spectrum ($CDCl_3$, δ, ppm): 0.53–0.82 m, 2H, 1.1–1.33 m, 2H, 1.85–2.33 m, 1H, 7.1–7.4 m, 15H, 7.50 and 7.66, 2H, 7.97 s and 8.10 s, 2H. ^{13}C NMR spectrum, see Table 1.

Lithium diisopropylamide [21]

To diisopropylamine dissolved in absolute THF and cooled down to − 60 °C equimolar amount of n-butyllithium in hexane was added under argon. After stirring for 20 min at − 60 °C, the compound to be metallated, dissolved in absolute THF was added to the resulting solution of $i\text{-}Pr_2NLi$.

1-Triphenylphosphinegold-1-diethylcarbamoylcyclopropane (VII)

A solution in hexane of lithium diisopropylamide in 8 ml of absolute THF was prepared as described above from 0.31 ml (2.2 mmol) diisopropylamine and 0.9 ml of 2.35 *N* solution of n-butyllithium (2.1 mmol) in hexane. Compound IV (0.28 g, 2.0 mmol) [22] in 4 ml of absolute THF was added dropwise at − 65 ° C and mixed for 1.5 h. The suspension of I (1.0 g, 0.67 mmol) in 15 ml of absolute THF was then added to the reaction mixture. After 20 min the mixture reached room temperature and the stirring was continued for an additional 30 min till the oxonium salt dissolved. The reaction mixture was then decomposed with a small amount of water, the organic layer was separated, dried with K_2CO_3, filtered, and evaporated in vacuo. The residue was washed with a solvent mixture of light petroleum, and benzene. Hexane was then added and the turbid solution was filtered. The filtrate was dissolved with hexane. The crystals precipitated were separated and reprecipitated from a mixture of acetone and light petroleum to yield 0.40 g (33%) of VII as white crystals, m.p. 175–176 ° C. Found: C, 52.36; H, 4.92; N, 2.28; P, 5.20; Au, 33.11. $C_{26}H_{29}AuPON$ calcd.: C, 52.09; H, 4.88; N, 2.35; P, 5.17; Au, 32.86%. IR (cm^{-1}): 3100w, 1600s, 1320w, 1290s, 1160w, 1108s, 1000m, 760m, 750m, 715m, 700m, 614w, 537s, 505s. ^1H NMR (C_6D_6, δ, ppm): 1.13m (^2J 7 Hz), 6H, 1.40–1.67m, 4H, 3.47q (^2J 7 Hz), 2H, 3.93q (^2J 7 Hz), 2H, 6.83–7.50m, 15H. ^{13}C NMR spectrum, see Table 1.

1-Triphenylphosphinegold-1-diethylcarbamoyl-2-phenylcyclopropane (VIII)

A solution of lithium diisopropylamide in absolute THF was prepared as described above from 0.33 ml (2.4 mmol) of diisopropylamine and 1.05 ml of 2.35 *N* n-butyllithium (2.4 mmol) in hexane. *cis*-2-Phenylcyclopropanecarboxylic acid diethylamide (0.5 g, 2.3 mmol) dissolved in 5 ml of absolute THF was added dropwise at − 70 ° C. The mixture obtained was mixed for 1 h at − 70 ° C, and then the suspension of I (1.0 g, 0.67 mmol) in 20 ml of absolute THF was added. In about 20 min the mixture was heated to − 20 ° C, stirred for an additional 40 min at − 10 to − 20 ° C, and then 5 ml of cold water and potassium carbonate were added in succession. The organic layer was separated, dried with K_2CO_3, filtered, and evaporated. The residue was washed several times with small portions of pentane (3–5 ml) dissolved in ether. Pentane was then added and the turbid solution formed was filtered. Ether was evaporated in vacuo without heating, and the residue was dried in high vacuo. 1.2 g of VIII (89%) was isolated which is according to ^{13}C NMR a mixture of *cis* and *trans* isomers. Found: C, 57.23; H, 4.70; N, 2.17; P, 4.56. $C_{32}H_{33}NOAuP$. calcd.: C, 56.89; H, 4.92; N, 2.07; P, 4.58%. IR (cm^{-1}): 3100w, 1605s, 1275s, 1186w, 1150w, 1104s, 1085m, 1003m, 760s, 710s, 700s, 535s, 510s.

Under the same conditions, we obtained from *trans*-2-phenylcyclopropane carboxylic acid diethylamide the mixture of *cis*- and *trans*-1-triphenylphosphinegold-1-diethylcarbamoyl-2-phenylcyclopropanes. The ^{13}C NMR spectrum of the mixture was identical with that of the mixture isolated in the previous case.

Lithium salt of bis(1-diethylcarbamoylcyclopropyl)aurate (XII)

A solution of lithium diisopropylamide in 8 ml of absolute THF was prepared as described above from 1.12 ml (9 mmol) of diisopropylamine and 3.64 ml of 2.2 *N* n-butyllithium (8 mmol) in hexane. Cyclopropanecarboxylic acid diethylamide (1.13 g, 8 mmol) dissolved in 5 ml of absolute THF was slowly added at − 70 ° C. The mixing was continued for 1.5 h and then a suspension of I (1.0 g, 0.67 mmol) in 15 ml of absolute THF was added. The temperature of the reaction mixture was gradually increased to the room temperature and the mixture was stirred for 1 h.

When the reaction was over, the mixture was decomposed with 5 ml of water, the aqueous layer was separated (for better separation sodium sulfate was added), the organic layer was dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was washed several times with hexane (4 × 5 ml) to remove an excess of the starting diethylamide and triphenylphosphine liberated. The residue was then dissolved in absolute benzene, filtered, and the filtrate was diluted with light petroleum. The hydrate $[(\overline{CH_2CH_2C})CON(CH_2CH_3)_2]_2AuLi \cdot 1.5H_2O$ (XII) was isolated in 83% yield (0.80 g). XII decomposes on storing in the air within several days and under the action of non-absolute solvents. Found: C, 37.64; H, 6.18; N, 5.18. $C_{32}H_{64}Au_2N_4O_7$ calcd.: C, 37.58; H, 6.11; N, 5.48%. The presence of lithium was qualitatively confirmed from analysis of an aqueous solution of XII on a Flapho 4 flame photometer. The IR spectrum contains a broad band at 3400 cm^{-1} ascribed to the OH group and a band at 1570 cm^{-1} corresponded to the carbonyl group. ^1H NMR (C_6D_6/py-d_5 2/1, δ, ppm) 0.8–1.47m, 10H, 3.30q (J 7 Hz), 2H, 3.98q (J 7 Hz), 2H, 4.83s, 3H.

Potassium salt of bis(1-diethylcarbamoylcyclopropyl)aurate (XIV)

The reaction was performed as described above for the lithium salt. After the decomposition of the reaction mixture with water K_2CO_3 was added and the aqueous layer was separated. The organic layer was dried with K_2CO_3. When the solution began to become turbid, it was quickly filtered through a porous glass filter. The fine suspension obtained was evaporated in vacuo. The residue was washed many times with small quantities of hexane to remove triphenylphosphine and unreacted cyclopropanecarboxylic acid diethylamide and then washed several times with chloroform. 0.36 g of XIV (70%) was obtained from 0.57 g IV. M.p. 245–247 °C with dec. Found: C, 37.80; H, 5.68; Au, 38.38; N, 5.70. $C_{16}H_{28}AuN_2O_2K$ calcd.: C, 37.21; H, 5.73; Au, 38.14; N, 5.43%. The presence of potassium was qualitatively demonstrated as above for the lithium salt.

Compound XIV is a fine white powder, practically insoluble in organic solvents. It is stable in the air for a long period of time but decomposes on contact with water.

IR (cm^{-1}): 3100w, 1575s, 1330m, 1300s, 1230m, 1150m, 1120s, 1080m, 950m, 880m, 790w, 700w, 610w. PMR (DMSO-d_6, δ, ppm): 0.83–1.67m, 10H, 3.42q (J 7 Hz), 2H, 4.13q (J 7 Hz), 2H.

Potassium salt of bis(1-diethylcarbamoylcyclopropyl)aurate (XIV) from 1-triphenylphosphinegold-1-diethylcarbamoylcyclopropane (VII)

A solution of lithium diisopropylamide in absolute THF was prepared from 0.31 ml (2.2 mmol) of diisopropylamine and 0.9 ml of 2.35 N n-butyllithium (2.1 mmol) in hexane. A solution of cyclopropanecarboxylic acid diethylamide (0.28 g, 2 mmol) in 4 ml of absolute THF was added dropwise at − 60 °C. Subsequently, a solution of VII (0.60 g, 1 mmol) in 20 ml of absolute THF was slowly added. The mixture was stirred for 0.5 h at − 70 °C and then warmed to room temperature mixing for an additional 0.5 h. When the reaction had ceased, 5 ml of water, then K_2CO_3 were added. The organic layer was separated and dried over potash. When the solution grew turbid, it was filtered through a porous glass filter and evaporated. The residue was washed with light petroleum, treated with benzene. The benzene solution was filtered and diluted with hexane. 0.25 g of unreacted complex VII was isolated, m.p.

175–176 ° C. The in benzene insoluble precipitate was washed with absolute chloroform. 0.25 g (83% based on VII reacted) of XIV was isolated, m.p. 245–247 ° C.

Lithium salt of bis(1-diethylcarbamoyl-2-phenylcyclopropyl)aurate (XIII)

A. From cis-2-phenylcyclopropanecarboxylic acid diethylamide (V). A solution of LDA in absolute THF was prepared from 0.62 ml (4.4 mmol) of diisopropylamine and 1.9 ml of 2.2 *N* n-butyllithium (4.18 mmol) in hexane. A solution of V (0.87 g, 4 mmol) in 6 ml of absolute THF was added dropwise at − 60 ° C. A suspension of I (0.50 g, 0.67 mmol) in 20 ml of absolute THF was added to the reaction mixture and the latter was warmed to room temperature, and stirred for 1 h. The colour of the solution turned dark-orange. The reaction mixture was decomposed with 5 ml of water and K_2CO_3 added. The organic layer was dried over potash, filtered, and the solvent was evaporated. The oil obtained was washed many times with pentane to extract triphenylphosphine liberated and unreacted V. The residue was dissolved in THF and pentane was added. The gelatinous precipitate was filtered, washed with pentane, and dried to give 0.33 g (49%) of XIII. Found: C, 52.83; H, 5.89; N, 3.93. $C_{28}H_{36}N_2O_2AuLi$ calcd.: C, 52.83; H, 5.70; N, 4.40%. IR: 1540 cm^{-1} (C=O).

B. From trans-2-phenylcyclopropanecarboxylic acid diethylamide (VI). The reaction was carried out as described above, but diethylamide (VI) was employed. The yield of XIII was 49% (0.33 g).

Interaction of potassium bis(1-diethylcarbamoylcyclopropyl)aurate (XIV) with hydrogen chloride in the presence of triphenylphosphine

To a solution of PPh_3 (0.13 g, 0.5 mmol) in 10 ml of benzene, XIV (0.26 g, 0.5 mmol) was added followed by dropwise addition of 5 ml of 0.1 *N* HCl (0.5 mmol). The reaction mixture was stirred for 10 min. The aqueous layer was separated, while the organic layer was dried with potash, filtered, and evaporated. The residue was washed with hexane and precipitated from a benzene/hexane mixture to yield 0.18 g of VII (60%), m.p. 175–176 ° C.

Interaction of potassium bis(1-diethylcarbamoylcyclopropyl)aurate (XIV) with water in the presence of triphenylphosphine

A. In THF. PPh_3 (0.07 g, 0.27 mmol) was dissolved in a mixture of THF (3 ml) and H_2O (0.2 ml). XIV (0.1 g, 0.2 mmol) was then added and the resulting solution was stirred for 3 h and allowed to stand overnight. The mixture was dried with potash, filtered, and the solvent was evaporated. The residue was extracted with benzene and VII was precipitated by addition of hexane to give 0.01 g (9%) of compound VII, m.p. 175–176 ° C.

B. In pyridine. Triphenylphosphine (0.11 g, 0.38 mmol) was dissolved in a mixture of pyridine (3 ml) and water (0.2 ml). XIV (0.2 g, 0.39 mmol) was then added and the resulting solution was kept at 35–40 ° C for 12 h, dried with potash, filtered, and the solvent evaporated in vacuo. The residue was washed with light petroleum and dissolved in benzene. The solution was filtered and diluted with hexane to afford 0.08 g (34%) of VII, m.p. 175–176 ° C.

Preparation of α-triphenylphosphinegold-N,N-diethylacetamide (XV)

A solution of LDA in absolute THF was prepared from 0.31 ml (2.2 mmol) of diisopropylamine and 1.1 ml of 2 *N* n-butyllithium (2.2 mmol) in hexane. A solution of diethylacetamide (0.25 g, 2.17 mmol) was added at – 70 ° C. The mixture was stirred for 45 min at – 65 ° C and a suspension of I (1 g, 0.67 mmol) in 20 ml of absolute THF was then added. Cooling was stopped and the reaction mixture was stirred for 40 min to achieve complete dissolution of the oxonium salt. When the reaction was completed, the reaction mixture was decomposed with water, the organic layer was separated and dried over potash, filtered and evaporated. The residue was washed with light petroleum and precipitated from benzene/hexane to obtain 0.78 g (67%) of XV as white crystals, m.p. 157–159 ° C with decomposition. Found: C, 50.51; H, 4.81; Au, 34.35; N, 2.58. $C_{24}H_{27}AuNOP$ calcd.: C, 50.27; H, 4.75; Au, 34.35; N, 2.44%. IR: 1590 cm^{-1} (C=O). PMR (CDCl$_3$, δ, ppm): 1.1t (*J* 7 Hz), 6H, 2.73d ($^3J(^{31}P-^1H)$ 11 Hz), 3.43q (*J* 7 Hz), 4H, 6.83–7.5 m, 15H.

Interaction of the lithium derivative of diethylacetamide with I at the ratio 4/1

A solution of LDA in absolute THF was prepared from 1.14 ml (8.2 mmol) of diisopropylamine and 4.1 ml of 2 *N* n-butyllithium (8.2 mmol) in hexane. A solution of diethylacetamide (0.98 g, 8.2 mmol) was added at – 70 ° C. The mixture obtained was stirred for 40 min at – 70 ° C and I (1.0 g, 0.67 mmol) in 20 ml of absolute THF was then added. The stirring was continued for 40 min at room temperature. Decomposition and further treatment of the reaction mixture were performed as in the previous case to yield 1.0 g (86%) of XV, m.p. 157–159 ° C with decomposition.

References

1 K.I. Grandberg, Usp. Khim., 51 (1982) 438.
2 J. March, Advanced Organic Chemistry Reactions, Mechanisms and Structure. 3rd edit., 1985, p. 143, 276, 283.
3 E.G. Perevalova, I.G. Bolesov, E.S. Zaichuk, A.N. Kosina, K.I. Grandberg, Koord. Khim., 10 (1984) 1040.
4 E.G. Perevalova, I.G. Bolesov, Yu.T. Struchkov, I.F. Leschova, Ye.S. Kalyuzhsnaja, T.I. Voyevodskaya, Yu.L. Slovokhotov, K.I. Grandberg, J. Organomet. Chem., 286 (1985) 129.
5 V.P. Dyadchenko, Vestn. MGU, Khimia, (1976) 358.
6 E.G. Perevalova, Yu.T. Struchkov, D.N. Kravtsov, L.G. Kuz'mina, E.I. Smislova, K.I. Grandberg, O.N. Kalinina, V.P. Dyadchenko, T.I. Voevodskaya, Zh. Obsh. Khim., 58 (1988) 62.
7 O.A. Subbotin, A.S. Kozmin, Yu.K. Grishin, N.M. Sergeev, I.G. Bolesov, Org. Magn. Reson., 4 (1972) 53.
8 D.E. Applequist, A.H. Petersen, J. Am. Chem. Soc., 83 (1961) 862.
9 H.M. Walborsky, F.J. Impastato, A.E. Young, J. Am. Chem. Soc., 86 (1964) 3283.
10 G.W. Rice, R.S. Tobias, Inorg. Chem., 15 (1976) 489.
11 R.W. Baker, P.J. Pauling, J. Chem. Soc., Dalton Trans., (1972) 2264.
12 X. Solans, G. Miravittles, J.M. Arrieta, G. Germain, J.F. Declercq, Acta Cryst. B, 38 (1982) 1812.
13 E.G. Perevalova, Yu.T. Struchkov, V.P. Dyadchenko, E.I. Smislova, Yu.L. Slovokhotov, K.I. Grandberg, Izv. AN SSSR, Ser. Khim., (1983) 2818.
14 F.H. Allen, Acta Crystallogr., B, 36 (1980) 81.
15 M. Brookhart, M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.
16 M. Burke-Laing, M. Laing, Acta Crystallogr. B, 32 (1976) 3216.
17 E.L. Sutton (Ed.), Tables of interatomic distances and configuration in molecules and ions, London, Chem. Soc., Special Publication, 1965, No. 18.
18 V.I. Korsunsky, J. Organomet. Chem., 311 (1986) 367.
19 M.Yu. Lukina, Usp. Khim., 31 (1962) 901.
20 G. Van Koten, J.T.B.H. Jastrzebski, C.H. Stam, N.C. Niemann, J. Am. Chem. Soc., 106 (1984) 1880.
21 R.W. Ihies, R.H. Chiarello, J. Org. Chem., 44 (1979) 1342.
22 E.T. McCabe, W.F. Barthel, S.I. Gertler, S.A. Hall, J. Org. Chem., 19 (1954) 493.