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SYNTHESIS, STRUCTURE AND SOME PROPERTIES OF AURATED DERIVATIVES OF DICYCLOPROPYL KETONE

E.G. PEREVALOVA, I.G. BOLESOV *, Yu.T. STRUCHKOV, I.F. LESCHOVA, Ye.S. KALYUZHNAYA, T.I. VOYEVODSKAYA, Yu.L. SLOVOKHOTOV and K.I. GRANDBERG

Laboratory of Organo-Element Compounds, Chemistry Department, M.V. Lomonosov Moscow State University, Moscow 117234 (U.S.S.R.)

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Summary

The reaction of the lithium-containing derivative of dicyclopropyl ketone with chloro(triphenylphosphine)gold has been shown to produce two organogold derivatives of the cyclopropane series. The lithium-containing derivative of dicyclopropyl ketone was obtained by treating dicyclopropyl ketone with lithium diisopropylamide. Depending on the molar ratio of the starting ketone and lithium diisopropylamide, the reaction of auration proceeds by two different modes: with the formation of aurated dicyclopropyl ketone or aurated tetracyclopropyl hydroxyketone. Dicyclopropyl ketone undergoes aldol condensation in the presence of lithium diisopropylamide. All the compounds synthesized were characterized by IR, ^{1}H and ^{13}C NMR spectroscopic data. The structure of aurated dicyclopropyl ketone was determined by X-ray crystal analysis.

Introduction

Cyclopropane derivatives represent part of the rapidly developing chemistry of small ring molecules. Numerous investigations of the chemistry of strained compounds of this type, in which the structural and quantum-chemical data of such molecules are often discussed, has allowed some conclusions to be made concerning their reactivity and structural features [1–3].

It should be noted that the properties of metallated derivatives of the cyclopropane series are not very well known and the stereochemical consequences of a metal atom bonding to a three-membered ring have not been fully explored. This work is a continuation of the studies of aurated derivatives of cyclopropane which have a small carbon ring and a gold atom capable of coordinating with organic ligands in the unusual manner. Considering the known properties of metallic gold and its complexes, one should take notice of its catalytic activity, which differs from that of other metals of Group I and their complexes. In particular, this refers to the catalytic

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rearrangements of diademane [4], benzvalene [5], and bicyclo[1.1.0]butane [6].

Previously we have investigated the reactions of acetylcyclopropanes with tris(triphenylphosphinegold)oxonium tetrafluoroborate (I) in the presence of an alkaline agent [7]. In these reactions, the small cycle did not open and auration led to the formation of (triphenylphosphinegoldmethyl)cyclopropyl ketones. The cyclopropane ring was not involved in the reactions. Keeping in mind this result, in the present study we chose dicyclopropyl ketone (II) as the starting compound. The molecular structure of II precludes the possibility of the competing route of the auration reaction mentioned above. However, it was found that the dicyclopropyl ketone was not aurated by tris(triphenylphosphinegold)oxonium tetrafluoroborate in the presence of sodium hydride. After stirring for 3 h, the reaction mixture contained only the starting compounds. Therefore in order to synthesize the organogold derivative of dicyclopropyl ketone, we decided to use the other traditional method of synthesizing complexes with a σ-gold–carbon bond, which includes the interaction of an organolithium compound with the triphenylphosphine complex of monovalent gold chloride.

To do this, it was necessary to obtain (1-lithiumcyclopropyl)cyclopropyl ketone and to introduce it into the reaction with chloro(triphenylphosphine)gold (III). However, as is known, the most active organometallic compounds attack the carbon atom of the carbonyl group of dicyclopropyl ketone. A variety of reagents including dichloromethyllithium [8], sodium acetylide [9], isopropylmagnesium bromide [10], cyclopropyllithium [11], the lithium salt of α-lithiated isobutyric acid [12] add to the carbonyl group of II to produce (after hydrolysis) the correspondingly substituted derivatives of dicyclopropyl carbinol. It is evident that the problem of choosing reagents which are able to metallate dicyclopropyl ketone requires particular consideration.

The reagents in question should satisfy certain requirements. Firstly, they should be strong bases. It is known that acylcyclopropanes have an acidity that is 1 to 3 orders of magnitude below than that of alkyl ketones [13]. For example, dicyclopropyl ketone cannot be deprotonated under the conditions usually used for enolization of aliphatic ketones. Attempts to demonstrate H–D exchange in dicyclopropyl ketone using an $NaOD/D_2O/DMF$ mixture at 60°C for 30 h or a t-BuOD/t-BuOK mixture at 35°C for 480 h have failed [14]. An attempt to enolize dicyclopropyl ketone using lithium and sodium hydrides in tetrahydrofuran (THF) was also unsuccessful. Potassium hydride in THF adds to dicyclopropyl ketone, forming a good yield of dicyclopropyl carbinol. α-Deuterated dicyclopropyl ketone was obtained by the interaction of dicyclopropyl ketone with sodium methylate in methanol followed by decomposition with deuterium oxide [15]. However, the data published lack information concerning the introduction of other substituents, alkylic, acyclic, or organoelement, to the α-carbon atom of dicyclopropyl ketone.

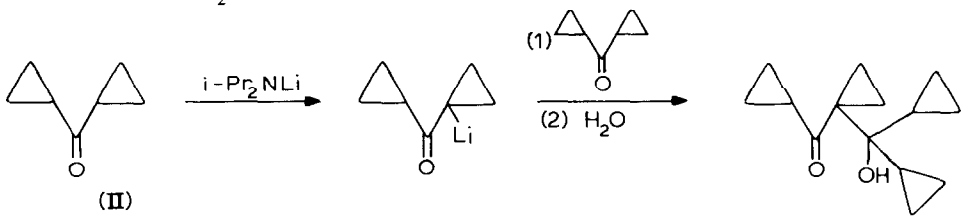
Secondly, the structural features of the metallating reagents must be such that they prevent the reaction proceeding at the carbonyl group of II.

Lithim diisopropyl amide ($i\text{-}Pr_2NLi$) meets these two requirements. Its reaction centre is sterically hindered. We believed that the two large isopropyl groups of $i\text{-}Pr_2NLi$ would prevent the reaction proceeding at the relatively inaccessible carbonyl group of II. The metallating reaction with a neighbouring hydrogen atom seemed to be more probable. This reaction, followed by interaction with chloro(triphenylphosphine)gold, could yield an organogold compound.

Results and discussion

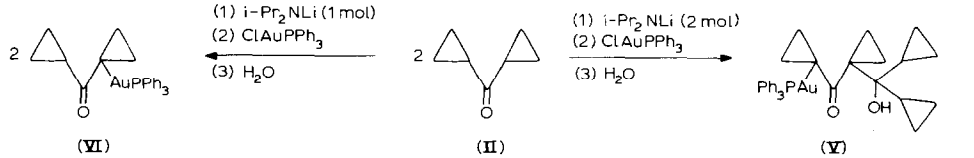
First we investigated the interaction of dicyclopropyl ketone with i-Pr_2NLi because the possibility of the reaction with participation of the carbonyl fragment occurring could not be excluded. The reaction of II with i-Pr_2NLi was carried out in ether or in THF for 1 h. The isolated reaction product was a viscous, high-temperature boiling liquid, whose elemental analysis data were identical to those of dicyclopropyl ketone, but it had different physico-chemical properties. The IR spectrum of the synthesized compound showed the presence of two functional groups in its molecule: a carbonyl (very strong band at 1660 cm^{-1}) and a hydroxyl (broad band at 3450 cm^{-1}). Its structure was determined by ^{13}C NMR spectroscopy.

We suggest that the most probable mechanism of this reaction includes abstraction of a proton next to the carbonyl group, upon action of i-Pr_2NLi at dicyclopropyl ketone. Then the lithium derivative of II reacts with the carbonyl group of II to produce hydroxyketone IV. This means that aldol condensation of dicyclopropyl ketone, previously unknown for this ketone, occurs. This process is quite usual for most other ketones, but it is very difficult to carry out in this case when reagents different from i-Pr_2NLi are used.



(II) (IV)

Then the reaction of the lithium derivative of dicyclopropyl ketone with chloro(triphenylphosphine)gold was investigated. It was found that, depending on the ratio of the reagents, this reaction may proceed by different routes. For example, when chloro(triphenylphosphine)gold was added directly to the reaction mixture after the reaction of equimolar amounts of dicyclopropyl ketone and i-Pr_2NLi was completed, a good yield of the organogold derivative V was obtained. In this compound, the gold atom is bonded to the α-carbon atom of the cyclopropane ring *. The reaction of a two-fold excess of dicyclopropyl ketone with i-Pr_2NLi gave an other product, aurated dicyclopropyl ketone (VI).

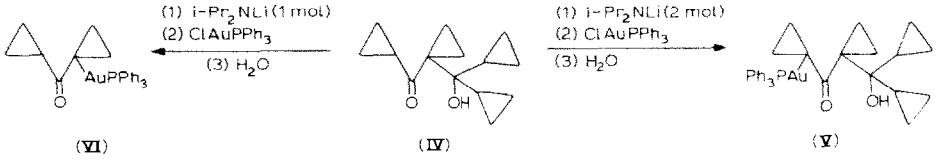


(VI) (II) (V)

When the previously isolated product of condensation, IV, which in turn had been treated with i-Pr_2NLi, was introduced into the reaction with chloro(triphenylphosphine)gold, two different compounds were formed too: namely, for a two-fold

* Organogold derivative V can also be obtained by using tris(triphenylphosphinegold)oxonium tetrafluoroborate instead of chloro(triphenylphosphine)gold. This reaction has the same advantages: a shorter reaction time, a simpler method of purification, and a larger product yield.

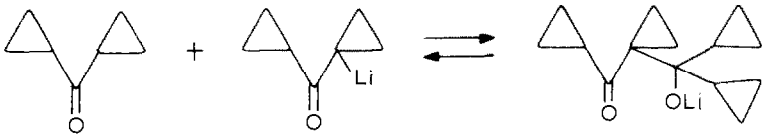
molar excess of i-Pr_2NLi, compound V was formed, and for an equimolar ratio of IV and i-Pr_2NLi, the product VI was isolated.



(VI) (IV) (V)

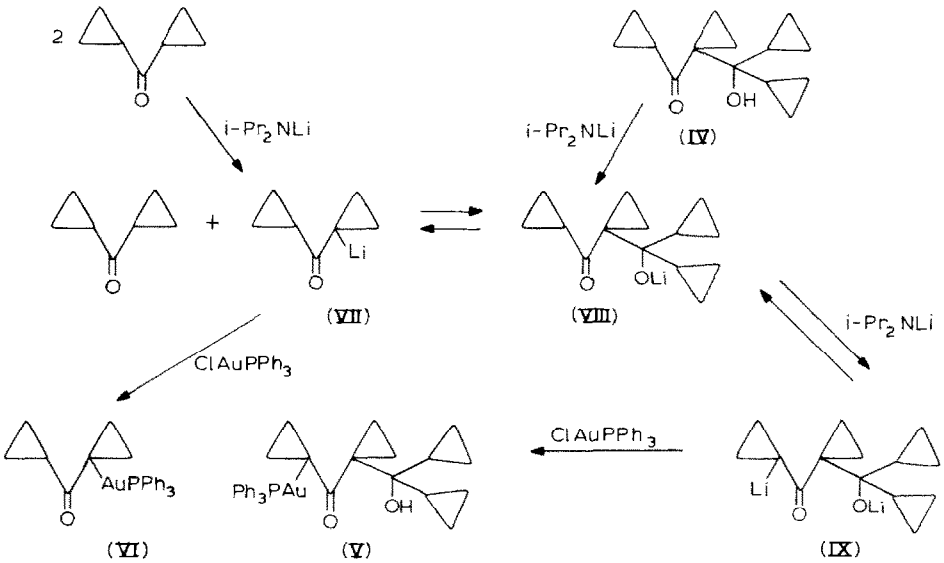
For intermediate ratios of IV and i-Pr_2NLi in the reaction mixture, a composite of V and VI was obtained, which could be separated by a number of successive precipitations, owing to lower solubility of VI in organic solvents.

To interpret these somewhat unexpected results, we have suggested that the process of condensation is reversible and that the concentration of i-Pr_2NLi influences the equilibrium:



On the basis of the results obtained, Scheme 1 of the product formation can be represented.

SCHEME 1



(VI) (V) (IX)

For marginal reagent ratios, that is for IV/i-Pr_2NLi 1/1 and II/i-Pr_2NLi 2/1, the predominant species in solution is the derivative VII; for ratios IV/i-Pr_2NLi 1/2 and II/i-Pr_2NLi 1/1, derivative IX is the predominant product. Correspondingly for intermediate ratios of reagents in the reaction mixture, both derivatives VII and IX are present in comparable concentrations. We revealed their presence by adding chloro(triphenylphosphine)gold to the reaction mixture. The remarkable stability of

the small ring in the variety of reactions mentioned above deserves to be noted.

Thus the method suggested allows preparative quantities of α-gold derivatives of dicyclopropyl ketone to be synthesized. Moreover, this method is of interest because of the possibility of synthesizing other derivatives (such as α-alkyl, α-organoelement, for example) of this compound.

The synthesized organogold derivatives V and VI of dicyclopropyl ketone are white, crystalline compounds, which are stable in air for a long time and are soluble in most organic solvents. As in other organogold complexes, the gold–carbon bond of these compounds is cleaved under the action of concentrated hydrochloric acid to give chloro(triphenylphosphine)gold [16].

Certain features of the IR spectra of compounds V and VI deserve to be mentioned. All the absorption bands of their functional groups are shifted considerably to lower field compared with similar bands in the starting non-aurated compounds. The value of the frequency shift of the carbonyl group is equal to 55 cm^{-1} (for compound V) and 40 cm^{-1} (for compound VI). The hydroxyl band shift of compound V is 90 cm^{-1}. Similar frequency shifts have previously been observed in other organogold species [17].

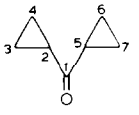
^{13}C NMR spectra

To elucidate the structures of compounds IV to VI, their ^{13}C NMR spectra have been studied. The ^{13}C chemical shifts are given in Table 1. The shifts were assigned using published data for substituted cyclopropanes [18], and were verified by the multiplet structure of the signals in the off-resonance spectra of compounds IV and V.

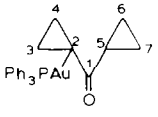
The spectrum of IV contains a signal for the C(1) atom of the carbonyl group (δ

TABLE 1

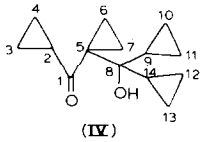
^{13}C CHEMICAL SHIFTS AND ^{13}C–^{31}P COUPLING CONSTANTS OF COMPOUNDS II AND IV–VI



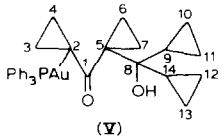
(II)



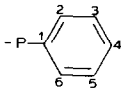
(VI)



(IV)



(V)

Compound	C(1)	C(2)	C(3,4)	C(5)	C(6,7)	C(8)	C(9,14)				
								C(1)	C(2,6)	C(3,5)	C(4)
II [a]	209.1	20.7	10.3	20.7	10.3						
VI	215.9	48.9	10.47	21.36				130.7	133.9	128.8	131.1
	(0.5)	(105.7)	(2)					(51)	(13.8)	(11)	(3)
IV	212.9	15.6	11.1	39.7	10.98	70.5	17.5				
V	220.0	45.7	11.5	37.3	9.9	70.8	17.8		133.8	128.9	131.3
		(102.9)							(14)	(10)	

[a] Lit. data [18].

212.9 ppm), signals for C(5), C(8) and C(9,14) (δ 39.7 ppm, 70.5 ppm, and 17.5 ppm, respectively), and a group of signals for the CH_2 groups of the cyclopropane rings in the range from 11 to −1 ppm (detailed assignment of these signals was not performed).

In the ^{13}C NMR spectrum of aurated compound V, the signals for C(1) and C(2) are shifted to low field (the displacements being equal to −7.1 ppm for C(1) and 30.1 ppm for C(2)) and the spin–spin coupling constant $^2J(^{13}C-^{31}P)$ 102.9 Hz is observed. This indicates that the $AuPPh_3$ group is bonded to the C(2) atom of compound V. Similar displacements of the chemical shifts and the appearance of the $^2J(^{13}C-^{31}P)$ constant for organogold derivatives were observed earlier [19]. There is also a group of signals in the range from 140 to 128 ppm which is assigned to the carbon atoms of the phenyl rings of the PPh_3 group of V.

The ^{13}C NMR spectrum of compound VI recorded at room temperature reveals four doublets in the range from 140 to 128 ppm, corresponding to the carbon atoms of the phenyl rings of the PPh_3 groups; no resonance signal of the C(2) atom is observed. Decrease of the temperature to −12°C leads to the appearance of a signal at δ 48.9 ppm and $^2J(^{13}C-^{31}P)$ 105.7 Hz. The spin–spin coupling constants $^3J(^{13}C-^{31}P)$ for atoms C(3,4) and C(1) are 2 and 0.5 Hz, respectively. Slow increase of the temperature to 0°C leads to broadening of the components of the signal of the C(2) atom. At room temperature, complete disappearance of the signal for C(2) and of the $^3J(^{13}C-^{31}P)$ constants was observed. The temperature dependence of the spectrum indicates the fast intermolecular exchange of PPh_3 groups at room temperature.

To elucidate the molecular and three-dimensional structures of VI and its metallated cyclopropane fragment, single crystals of VI were prepared and an X-ray structural study was carried out.

Geometry of molecule VI

Previous investigations of the molecular and electronic structures of substituted cyclopropanes revealed conjugation of the electron systems of the substituent and "banana-type" bonds of the three-membered ring [1,2]. In his review of the results of 91 accurate structural studies conducted at the Cambridge Crystallographic Data Base, Allen [3] reported in 1980 a quantitative analysis of the small (0.010–0.030 Å) variations of bond lengths in cyclopropane rings. Consideration of the frontier orbitals leads to the conclusion on the transfer of electron density from the HOMO of the cyclopropane system to the antibonding orbital of the π-acceptor substituent in its energetically most favourable "perpendicular" conformation when the anti-symmetry plane of the substituent π-system is perpendicular to the plane of three-membered carbocyclic ring. This electron density transfer results in elongation of the vicinal C_α–C_β bonds and shortening of the "distal" C_β–C_β' bond in the ring. Such a simple qualitative model fails to describe in details the interaction between other types of substituents and the MO system of cyclopropane [1]. However, according to the results of MO calculations, π-donor substituents in the "perpendicular" conformation give rise to the elongation of the C_β–C_β' bond, whereas the electronic influence of the substituent π-system in the "parallel" conformation is very weak and the effects of donor and acceptor σ-substituents are opposite to those of π-systems [20].

There are two three-membered rings, a strong π-acceptor (carbonyl group) and a

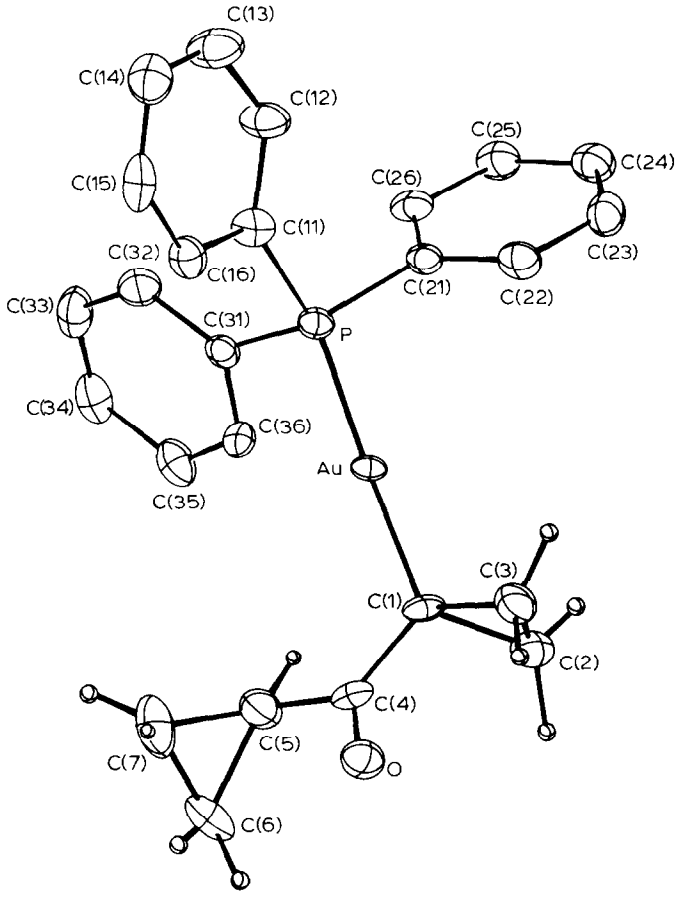


Fig. 1. Molecule VI (the hydrogen atoms of the Ph substituents have been omitted).

electropositive σ-donor substituent (Ph_3PAu) in the molecule of monoaurated dicyclopropyl ketone, $Ph_3PAuC_3H_4C(O)C_3H_5$ (VI). Therefore the geometrical parameters of the molecule should undergo considerable changes in comparison with standard values.

In molecule VI (Fig. 1), the linearly coordinated Au atom is bonded to one of the bridge-head carbon atoms of the dicyclopropyl ketone moiety. The bond lengths in VI are given in Table 2; the most important bond angles and torsion angles are listed in Table 3. The Au–C(1) bond length of 2.065(5) Å is close to the values found in mononuclear triphenylphosphine derivatives of Au^I with acceptor organic σ-ligands: 2.07(2) Å in $C_6F_5AuPPh_3$ [21], 2.062(9) Å in $Ph_3PAu(o\text{-}C_6Cl_4)PtCl(PPh_3)_2$ [22] and 2.05(1) Å in $Ph_3PAuC(CN)Cl_2$ [23]. The Au–P bond length of 2.281(1) Å is unexceptional (in the compounds mentioned above 2.27(1), 2.295(3) and 2.281(5) Å, respectively). The H[C(5)] atom at the bridge-head carbon atom in the non-aurated cyclopropyl substituent is orientated towards the Au atom. The slightly shortened Au...H[C(5)] distance of 2.94(9) Å possibly corresponds to a weak "secondary" interaction (taking into account the systematic effective shortening of the C–H bond length and the large errors in the hydrogen atom positions in X-ray structural

TABLE 2

BOND LENGTHS d(Å) IN VI

Bond	d	Bond	d
Au–P	2.281(1)	C(13)–HC(13)	0.99(6)
Au–C(1)	2.065(5)	C(14)–C(15)	1.380(8)
Au–HC(5)	2.94(9)	C(14)–HC(14)	0.92(6)
P–C(11)	1.820(5)	C(15)–C(16)	1.386(8)
P–C(21)	1.818(5)	C(15)–HC(15)	0.93(5)
P–C(31)	1.805(6)	C(16)–HC(16)	0.98(5)
O–C(4)	1.234(6)	C(21)–C(22)	1.400(7)
C(1)–C(2)	1.537(8)	C(21)–C(26)	1.389(8)
C(1)–C(3)	1.507(8)	C(22)–C(23)	1.395(8)
C(1)–C(4)	1.468(7)	C(22)–HC(22)	1.00(4)
C(2)–C(3)	1.468(9)	C(23)–C(24)	1.375(8)
C(2)–HC(2.1)	0.94(5)	C(23)–HC(23)	0.78(7)
C(2)–HC(2.2)	0.98(7)	C(24)–C(25)	1.393(9)
C(3)–HC(3.1)	1.00(6)	C(24)–HC(24)	0.97(5)
C(3)–HC(3.2)	1.05(7)	C(25)–C(26)	1.386(8)
C(4)–C(5)	1.487(8)	C(25)–HC(25)	1.07(5)
C(5)–C(6)	1.514(8)	C(26)–HC(26)	1.09(5)
C(5)–C(7)	1.515(9)	C(31)–C(32)	1.398(7)
C(5)–HC(5)	0.98(8)	C(31)–C(36)	1.395(8)
C(6)–C(7)	1.488(9)	C(32)–C(33)	1.365(9)
C(6)–HC(6.1)	1.05(6)	C(32)–HC(32)	0.91(5)
C(6)–HC(6.2)	0.99(8)	C(33)–C(34)	1.381(9)
C(7)–HC(7.1)	1.05(6)	C(33)–HC(33)	0.97(4)
C(7)–HC(7.2)	1.03(7)	C(34)–C(35)	1.377(9)
C(11)–C(12)	1.380(8)	C(34)–HC(34)	0.94(5)
C(11)–C(16)	1.386(8)	C(35)–C(36)	1.387(9)
C(12)–C(13)	1.377(8)	C(35)–HC(35)	0.85(8)
C(12)–HC(12)	0.97(5)	C(36)–HC(36)	0.91(7)
C(13)–C(14)	1.375(9)		

TABLE 3

VALENCE (ω) AND TORSION (τ) ANGLES (degrees) IN VI

Valence angles			
PAuC(1)	176.7(2)	C(1)C(4)O	123.2(5)
AuPC(11)	112.0(2)	C(5)C(4)O	118.4(5)
AuPC(21)	111.1(2)	C(1)C(4)C(5)	118.4(5)
AuPC(31)	116.4(2)	C(4)C(5)C(6)	118.8(5)
C(11)PC(21)	105.2(2)	C(4)C(5)C(7)	116.5(5)
C(11)PC(31)	105.6(2)	C(6)C(5)C(7)	58.9(4)
C(21)PC(31)	105.7(2)	C(5)C(6)C(7)	60.6(4)
AuC(1)C(2)	117.8(4)	C(5)C(7)C(6)	60.5(4)
AuC(1)C(3)	120.2(4)		
AuC(1)C(4)	119.7(4)	*Torsion angles*	
C(2)C(1)C(3)	57.7(4)	AuC(1)C(4)C(5)	29.0(5)
C(2)C(1)C(4)	110.8(4)	AuC(1)C(4)O	−150.2(7)
C(3)C(1)C(4)	114.9(5)	OC(4)C(1)C(2)	67.6(6)
C(1)C(2)C(3)	60.1(4)	OC(4)C(1)C(3)	4.6(6)
C(1)C(3)C(2)	62.2(4)	OC(4)C(5)C(6)	−20.3(6)
		OC(4)C(5)C(7)	47.0(7)

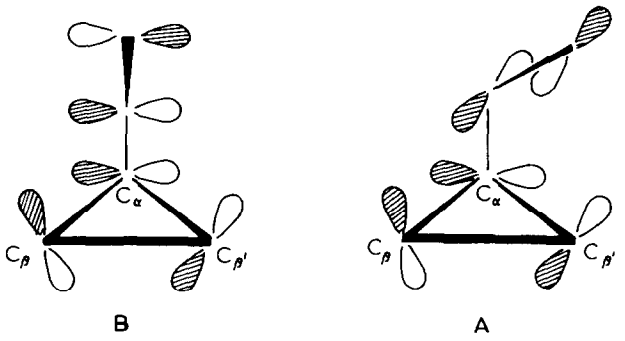


Fig. 2. Molecular orbitals of the conjugated cyclopropyl-carbonyl system in the bisectorial (ring B, left) and gauche (ring A, right) conformations.

investigations, the real value of the Au...H[C(5)] distance could be equal to 2.7–2.8 Å). The conformation of the AuC(1)C(4)C(5) and C(1)C(4)C(5)H(C5) fragments is close to cisoid, with the corresponding torsion angles being equal to 29.0(5)° and 10(2)°.

The dicyclopropyl ketone moiety differs slightly from the idealized C_{2h} symmetry. The latter demands a strictly perpendicular bisectorial conformation of the carbonyl group relative to the three-membered rings C(1)–C(3) (ring A) and C(5)–C(7) (ring B). However, both rings are found to be slightly rotated around their exocyclic C–C bonds, with the dihedral angle between the planes of rings A and B being 115.9° and the dihedral angles of these planes with the coordination plane of the sp^2-hybridized C(4) atom being 101.6 and 95.0°. Still the orientation of the carbonyl group remains close to the bisectorial confirmation relative to ring B (torsion angles OC(4)C(5)C(6) 20.3(6)° and OC(4)C(5)C(7) 47.0(7)°) and corresponds to a gauche conformation relative to ring A (torsion angles OC(4)C(1)C(2) 67.6(6)° and OC(4)C(1)C(3) 4.6(6)°). Due to steric repulsion between the O and C(3) atoms, which are in an eclipsed conformation, the bond angles at C(4) are somewhat distorted, viz. the OC(4)C(1) angle of 123.2(5)° is much larger than the OC(4)C(5) angle of 118.4(5)°.

The average C–C bond length of 1.505 Å in rings A and B is in good agreement with the average value of 1.504(3) Å in cyclopropane carbonyl derivatives (according to data on 27 structures) and is somewhat shorter than the C–C bond length of 1.5096(15) Å in unsubstituted cyclopropane [3]. The C_α–C_β bonds in ring B are elongated by 0.009 Å (C(5)–C(6)) and 0.010 Å (C(5)–C(7)), whereas the distal C(6)–C(7) bond is shortened by 0.017 Å in comparison with the mean value of 1.505 Å. The corresponding mean variations of the C–C bond lengths in the 20 cyclopropane carbonyl derivatives studied previously are equal to +0.010 Å (C_α–C_β) and −0.025 Å (C_β–$C_{\beta'}$). In ring A, inequality of the vicinal bond length increments is observed (+0.032 Å for C(1)–C(2) and +0.002 Å for C(1)–C(3)); this has also been noticed in other gauche-carbonylcyclopropane structures. The C(2)–C(3) bond is shortened by 0.037 Å, while the mean shortening in the seven gauche-structures mentioned above equals 0.023 Å.

The inequality of the C_α–C_β and C_α–C_β' bond lengths in ring A is probably due to the difference in conjugation of the corresponding HOMO components of cyclopropane with the π^*-MO of the carbonyl group in the gauche-conformation. In

this case, substantial overlapping (Fig. 2) is retained only for a gauche-orientated bond of the ring, while conjugation of its eclipsed counterpart, C_α–C_β', is considerably decreased. It should be noted that in all cases of a "pure" gauche-conformation the eclipsed bond of the three-membered ring (as in ring A of molecule VI) is not substantially shortened.

The shortening of the C(1)–C(4) and C(4)–C(5) bonds to 1.468(7) and 1.487(8) Å, respectively, and the elongation of the C(4)–O bond to 1.234(6) Å in comparison with the C–C and C=O bonds in alkyl ketones (in acetone 1.517(3) and 1.210(4) Å [24]) also indicate conjugation of the three-membered ring with the carbonyl group. Therefore a tendency of cyclopropane derivatives to exhibit "olefinic" properties is clearly observed in the structure of VI.

The influence of the Au atom on the bond length distribution in ring A is less evident, probably because metallated cyclopropyl derivatives have not been studied as thoroughly as their organic analogues. At the present time, besides the investigations of the disordered cyclopropyl thallium diisobutyrate [25] and the cyclopropyl derivative of cobaloxime [26], where significant errors do not justify a discussion of the bond lengths in three-membered rings, there are significantly accurate X-ray data on $(C_3H_5)_2Pt(PPh_2Me)_2$ [27] and $(C_3H_5)_4Al_2(\mu\text{-}C_3H_5)_2$ [28]. The structure of the platinum complex does not reveal any systematic bond length changes (varying in the range of 1.488–1.527 Å) in σ-cyclopropyl ligands, while in dimeric tri(cyclopropyl)aluminium a marked shortening of the C_β–C_β' bonds in the terminal cyclopropyl groups (C_α–C_β of 1.507 Å and C_β–C_β' of 1.463 Å averaged for three ordered C_3H_5 substituents), increasing in the bridging ligands (where the C_α–C_β and C_β–C_β' vicinal bonds are also elongated to 1.548 and 1.437 Å, respectively), is observed. In aurated ketone VI, the more pronounced shortening of the C_β–C_β' bond in ring A can be similarly explained by the joint action of the π-acceptor (CO) and σ-donor (Ph_3PAu) substituents, although the difference in the bond lengths, C(2)–C(3) of 1.468(9) Å and C(6)–C(7) of 1.488(9) Å, is within the limits of errors. The influence of the metal atom on the geometrical features of the σ-coordinated cyclopropane ring demands further structural investigations.

Experimental

IR spectra were recorded on an IKS-29 instrument in vaseline oil, ^1H NMR spectra were obtained on a Tesla B-497 spectrometer at a working frequency of 100 MHz, and ^{13}C NMR spectra were measured on either a CFT 20 or a FT 80 instrument using deuteriochloroform as the solvent.

1. 1-[(Dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone (IV)

30 ml of a 1.8 *N* (54 mmol) solution of n-butyllithium in petroleum ether was added to a cold solution of 7.7 ml (55 mmol) of diisopropylamine in 100 ml of absolute ether (at −60°C) in an argon flow. After stirring at −60°C for 15 min, the reaction mixture was allowed to reach room temperature, then a solution of 4 g (36 mmol) of dicyclopropyl ketone in 25 ml of absolute ether was added dropwise. The reaction mixture was stirred at room temperature for 1 h, then it was treated with water. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic portion was dried over anhydrous sodium sulphate, the solvent was removed by rotary evaporation, and the residue was distilled in vacuo to

yield 0.67 g (16%) of the starting dicyclopropyl ketone (b.p. 44–45°C/1 mmHg, n_D^{19} 1.4647) and 2.81 g (84%, based on the amount of dicyclopropyl ketone reacted) of [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone (b.p. 116–120°C/1 mmHg, n_D^{19} 1.5089). Found: C, 76.21; H, 9.42. $C_{14}H_{20}O_2$ calcd.: C, 76.32; H, 9.15%. The IR spectrum contains a very strong band at 1660 cm^{-1} (C=O group) and a broad band at 3450 cm^{-1} (OH group). ^1H NMR ($CDCl_3$, δ, ppm): 0.2–1.2 m, 4.35 s.

2. (1-Triphenylphosphinegoldcyclopropyl) [1-(dicyclopropylhydroxymethyl)cyclopropyl] ketone (V)

(a) Starting from dicyclopropyl ketone. 3.2 ml of a 2.6 *N* (8.3 mmol) solution of n-butyllithium in petroleum ether was added to a cold (−70°C) solution of 1.26 ml (9 mmol) of diisopropylamine in 15 ml of absolute THF in an argon flow. After stirring at −65°C for 0.5 h, the reaction mixture was allowed to warm to room temperature. Then a solution of 0.88 g (8 mmol) of dicyclopropyl ketone in 5 ml of absolute THF was added. The mixture was stirred for 0.5 h at room temperature, then a solution of 1 g (2 mmol) of chloro(triphenylphosphine)gold in 15 ml of absolute THF was added and stirring was continued for another hour. After the reaction was completed, the mixture was treated with water, the organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic layers were washed with water and dried over potassium carbonate, and the solvent was evaporated in vacuo. The residual oil was washed several times with petroleum ether. The solid residue was dissolved in ether, and the solution was filtered and diluted with hexane. 0.71 g (53% yield) of (1-triphenylphosphinegoldcyclopropyl) [1-(dicyclopropylhydroxymethyl)cyclopropyl] ketone was obtained, m.p. 136–139°C. Found: C, 56.68; H, 5.21; Au, 29.25. $C_{32}H_{34}O_2AuP$ calcd.: C, 56.64; H, 5.05; Au, 29.03%. IR (cm^{-1}): 3360, 1605, 1385, 1335, 1200, 1190, 1145, 1107, 1050, 1028, 939, 904, 890, 877, 830, 756, 729, 714, 700, 615, 600, 542, 511, 503.

(b) Starting from [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone. 1.5 ml of a 3 *N* solution (4.5 mmol) of n-butyllithium in hexane was added slowly, in a flow of argon, to a cold (−60°C) solution of 0.77 ml (5.5 mmol) of diisopropylamine in 8 ml of absolute ether. The mixture was stirred at −60°C for 20 min, then heated to room temperature in 10 min, and after that a solution of 0.44 g (2 mmol) of [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone in 5 ml of absolute ether was added and the mixture was stirred for 1.25 h. A solution of 0.5 g (1 mmol) of chloro(triphenylphosphine)gold in 10 ml of absolute THF was then added dropwise. Stirring was continued for a further hour. The reaction mixture was treated as described in the previous experiment (2a). 0.31 g (45% yield) of (1-triphenylphosphinegoldcyclopropyl) [1-(dicyclopropylhydroxymethyl)cyclopropyl] ketone (V) was obtained from an ether/hexane mixture.

3. (1-Triphenylphosphinegoldcyclopropyl) cyclopropyl ketone (VI)

(a) Starting from [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone. 0.73 ml of a 3 *N* solution (2.2 mmol) of n-butyllithium in petroleum ether was added slowly, in a flow of argon, to a cold (−60°C) solution of 0.31 ml (2.2 mmol) of diisopropylamine in 8 ml of absolute ether. The mixture was stirred at −60°C for 20 min, then heated to room temperature in 10 min, and a solution of 0.44 g of [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone (2 mmol) in 5 ml

of absolute ether was added slowly. After the reaction mixture had been stirred for 1.25 h, a solution of 0.5 g (1 mmol) of chloro(triphenylphosphine)gold in 10 ml of absolute THF was added dropwise, and stirring was continued for a further hour. When the reaction had finished, the mixture was treated with water, dried over K_2CO_3, and the solvent was removed in vacuo. The residue was washed with hexane, dissolved in an ether/benzene (1/1) mixture, then filtered and diluted with hexane. Obtained: from hexane, 0.05 g; from ether/benzene/hexane mixture, 0.35 g (total yield 0.4 g, 70%) of (1-triphenylphosphinegoldcyclopropyl) cyclopropyl ketone, m.p. 146–150°C (with decomposition). Found: C, 52.91; H, 4.50; Au, 35.06. $C_{25}H_{24}AuPO$ calcd.: C, 52.83; H, 5.05; Au, 34.65%. IR (cm^{-1}): 1640, 1372, 1320, 1247, 1107, 1096, 1065, 1026, 1004, 890, 865, 820, 790, 755, 716, 700, 538, 508, ^1H NMR (C_6D_6, δ, ppm): 0.4–0.66 m (2H), 1.14–1.32 m (2H), 1.38–1.58 m (2H), 2.48–2.76 m (1H), 6.78–7.44 m (15H).

(b) Starting from dicyclopropyl ketone. The reaction was conducted as described in the previous experiment (3a), but instead of [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone a solution of 0.44 g (4 mmol) of dicyclopropyl ketone in 5 ml of absolute ether was added to a solution of i-Pr_2NLi in ether. 0.35 g (60% yield) of (1-triphenylphosphinegoldcyclopropyl) cyclopropyl ketone (VI) was obtained.

4. Interaction of [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone with i-Pr_2NLi (1/1 ratio)

3 ml of a 1.75 *N* (5.4 mmol) solution of n-butyllithium in petroleum ether was added slowly, in a flow of argon, to a cold (−60°C) solution of 0.8 ml (5.7 mmol) of diisopropylamine in 15 ml of absolute ether. The mixture was stirred at −60°C for 25 min, then heated to room temperature in 15 min, and a solution of 0.88 g (4 mmol) of [1-(dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone in 5 ml of absolute ether was added slowly. After stirring for 3 h, a solution of 1 g (2 mmol) of chloro(triphenylphosphine)gold in 22 ml of absolute THF was added dropwise. Stirring was continued for another hour. The reaction mixture was treated as described in experiment (2a). 0.68 g of white crystals, a mixture of compounds V and VI (according to IR measurements), was obtained. 0.32 g of (1-triphenylphosphinegoldcyclopropyl) cyclopropyl ketone was isolated after two successive precipitations from a benzene/hexane mixture.

5. Synthesis of (1-triphenylphosphinegoldcyclopropyl)[1-(dicyclopropylhydroxymethyl)-cyclopropyl] ketone by the interaction of IV with tris(triphenylphosphinegold)oxonium tetrafluoroborate

1.5 ml of a 3 *N* (5.5 mmol) solution of n-butyllithium in petroleum ether was added slowly to a cold (−60°C) solution of 0.63 ml (4.5 mmol) of diisopropylamine in 8 ml of absolute ether in a flow of argon. The mixture was stirred at −60°C for 20 min. Then it was heated to room temperature in 10 min, and a solution of 0.44 g (2 mmol) of [1-dicyclopropylhydroxymethyl)cyclopropyl] cyclopropyl ketone in 5 ml of absolute ether was added slowly. After 1.25 h the temperature of the solution was raised to −30°C and a suspension of 0.50 g (0.35 mmol) of tris(triphenylphosphinegold)oxonium tetrafluoroborate in 25 ml of absolute THF was added. After stirring for 15 min at −10°C, the reaction mixture was treated with a small portion

of ethanol and then with water. The organic portion was separated and the aqueous layer was extracted with benzene. The combined organic portion was washed with water, dried over K_2CO_3, and the solvent was removed in vacuo. The solid residue was washed with hexane, dissolved in an ether/benzene mixture (1/1), then diluted with hexane. Obtained: from hexane, 0.05 g, from ether/benzene/hexane mixture, 0.39 g of (1-triphenylphosphinegoldcyclopropyl) [1-(dicyclopropylhydroxymethyl)-cyclopropyl] ketone (V); total yield, 0.44 g (65%).

6. Reaction of concentrated hydrochloric acid with (1-triphenylphosphinegoldcyclopropyl) [1-(dicyclopropylhydroxymethyl)cyclopropyl] ketone (V)

A solution of 0.3 g of V in 10 ml of $CHCl_3$ was shaken with 5 ml of concentrated HCl for 5 min. The organic layer was separated, washed with an aqueous solution of sodium carbonate, washed with water, dried over K_2CO_3, and the solvent was removed in vacuo. The solid residue was dissolved in a minimal portion of $CHCl_3$, and the solution was filtered and diluted with hexane. 0.2 g (90% yield) of chloro(triphenylphosphine)gold was obtained, m.p. 242–243°C (lit. 243–244°C [29]).

7. Reaction of concentrated HCl with (1-triphenylphosphinegoldcyclopropyl) cyclopropyl ketone (VI)

A solution of 0.13 g of VI in 6 ml of $CHCl_3$ was shaken with 3 ml of concentrated HCl for 5 min. The rest of the procedure was as described in the previous experiment. 0.14 g (90% of the theoretical value) of chloro(triphenylphosphine)gold was obtained.

8. Reaction of tris(triphenylphosphinegold)oxonium tetrafluoroborate with dicyclopropyl ketone

0.5 g (4.5 mmol) of dicyclopropyl ketone and 0.08 g of sodium hydride were added to a suspension of 0.20 g (0.135 mmol) of tris(triphenylphosphinegold)oxonium tetrafluoroborate in 10 ml of absolute THF. The mixture was stirred for 3 h, then the precipitate was filtered, dissolved in $CHCl_3$, and the solution was diluted with acetone. 0.17 g of starting tris(triphenylphosphinegold)oxonium tetrafluoroborate was obtained, m.p. 221–222°C (lit. 221–222°C [30]).

X-Ray structural study

Crystals of $Ph_3PAuC_3H_4\ C(O)C_3H_5$ (VI) are monoclinic, a 20.960(4), b 8.171(1), c 25.222(3) Å, β 96.36(1)°, space group $C2/c$, $Z = 8$. The unit cell parameters and intensities of 3748 independent reflections were measured with a four-circle Syntex $P2_1$ automatic diffractometer at −120°C (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max}$ 48°). 3294 Observed reflections with $I > 2\sigma(I)$ were used in the calculations. According to the method of ref. 31, an absorption correction was applied taking into account the real form of crystal. The structure was solved by the direct method using the MULTAN program and refined by full matrix least squares in anisotropic approximation to $R = 0.056$. Hydrogen atoms, located at this stage in the difference synthesis, were included in the refinement with isotropic thermal parameters. Finally, $R = 0.027$, $R_w = 0.034$ for 2952 independent reflections with $I > 5\sigma\ (I)$ (for all 3748 independent reflections $R = 0.047$, $R_w = 0.040$). The atomic coordinates and their thermal parameters are listed in Table 4. All calculations were carried out with an Eclipse S/200 minicomputer using INEXTL programs [32].

TABLE 4

ATOMIC COORDINATES ($\times 10^4$ for Au and P; $\times 10^3$ for H) AND THEIR THERMAL PARAMETERS IN THE FORM $T = \exp[-1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + \ldots + 2B_{23}b^*c^*kl)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Au	1689(1)	20789(3)	35835(1)	1.233(9)	1.517(9)	1.741(9)	0.242(8)	0.261(7)	−0.028(8)
P	11350(6)	8491(16)	37582(5)	1.32(5)	1.54(5)	1.72(5)	0.15(5)	0.20(4)	0.01(4)
O	−1415(2)	5144(5)	3713(2)	1.6(2)	2.1(2)	2.9(2)	0.4(1)	0.5(1)	−0.1(1)
C(1)	−693(2)	3204(6)	3380(2)	0.9(2)	1.8(2)	2.6(2)	0.3(2)	0.2(2)	0.7(2)
C(2)	−922(3)	3233(7)	2792(2)	2.6(3)	2.9(3)	2.0(2)	0.9(2)	0.0(2)	−0.2(2)
C(3)	−1255(3)	2209(7)	3164(2)	2.5(3)	2.2(3)	3.2(3)	0.2(2)	−0.4(2)	−0.4(2)
C(4)	−860(2)	4738(7)	3642(2)	1.3(2)	1.8(2)	1.8(2)	0.4(2)	0.2(2)	0.6(2)
C(5)	−334(3)	5844(7)	3835(2)	2.2(3)	1.9(2)	3.9(3)	−0.1(2)	0.0(2)	−0.4(2)
C(6)	−486(3)	7622(7)	3940(3)	3.1(3)	1.5(2)	3.7(3)	−0.2(2)	1.1(2)	−0.7(2)
C(7)	−365(4)	6486(9)	4395(3)	4.2(4)	3.7(3)	4.0(3)	−0.7(3)	−1.0(3)	−1.6(3)
C(11)	1775(3)	2335(6)	3871(2)	1.6(2)	1.7(2)	1.6(2)	0.2(2)	0.3(2)	−0.3(2)
C(12)	2285(3)	2125(7)	4235(2)	2.0(2)	2.4(3)	2.4(2)	0.3(2)	0.2(2)	0.3(2)
C(13)	2765(3)	3278(8)	4285(2)	2.0(3)	3.6(3)	2.3(2)	−0.2(2)	−0.6(2)	−0.8(2)
C(14)	2751(3)	4633(8)	3962(2)	2.4(3)	2.8(3)	2.6(3)	−0.9(2)	0.3(2)	−1.0(2)
C(15)	2244(3)	4859(7)	3597(2)	3.1(3)	2.1(2)	2.3(3)	−0.6(2)	0.6(2)	−0.3(2)
C(16)	1755(3)	3716(7)	3552(2)	1.8(2)	1.9(2)	2.2(2)	0.0(2)	−0.2(2)	−0.3(2)
C(21)	1363(2)	−367(6)	3198(2)	1.8(2)	1.4(2)	1.5(2)	0.2(2)	0.2(2)	0.3(2)
C(22)	1998(3)	−490(7)	3060(2)	1.8(2)	1.9(2)	1.7(2)	0.1(2)	0.4(2)	0.5(2)
C(23)	2139(3)	−1415(7)	2618(2)	1.9(2)	2.2(2)	2.5(2)	0.4(2)	0.4(2)	0.2(2)
C(24)	1666(3)	−2229(7)	2325(2)	3.1(3)	1.8(2)	1.9(2)	0.6(2)	0.5(2)	−0.3(2)
C(25)	1034(3)	−2119(7)	2464(2)	2.4(3)	2.5(3)	2.5(2)	−0.1(2)	−0.2(2)	−0.6(2)
C(26)	887(3)	−1183(7)	2897(2)	1.8(2)	2.6(3)	2.4(2)	0.3(2)	0.6(2)	−0.5(2)
C(31)	1196(2)	−509(7)	4321(2)	1.5(2)	2.0(2)	2.1(2)	−0.2(2)	0.5(2)	0.2(2)
C(32)	870(3)	−139(7)	4773(2)	2.0(2)	2.1(2)	1.8(2)	−0.2(2)	0.4(2)	−0.3(2)
C(33)	924(3)	−1131(8)	5207(2)	1.9(2)	3.5(3)	1.6(2)	−0.8(2)	0.6(2)	−0.4(2)
C(34)	1300(3)	−2521(8)	5216(2)	3.3(3)	2.9(3)	2.2(2)	−0.8(2)	0.0(2)	0.5(2)
C(35)	1619(4)	−2913(8)	4772(3)	4.7(4)	3.4(3)	2.9(3)	1.4(3)	0.7(3)	1.2(2)
C(36)	1570(3)	−1923(8)	4327(2)	4.4(3)	3.0(3)	2.3(3)	1.6(3)	1.3(2)	0.6(2)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
HC(12)	231(2)	122(7)	448(2)	2(1)	HC(13)	313(3)	308(7)	454(2)	3(1)
HC(14)	308(3)	536(7)	401(2)	2(1)	HC(15)	222(3)	575(7)	337(2)	2(1)
HC(16)	136(3)	385(7)	333(2)	2(1)	HC(22)	235(2)	5(5)	328(2)	1.2(9)
HC(23)	249(3)	−152(8)	254(3)	3(1)	HC(24)	176(2)	−291(5)	203(2)	1.8(9)
HC(25)	65(3)	−276(6)	226(2)	3(1)	HC(26)	38(3)	−97(7)	295(2)	2(1)
HC(32)	65(2)	82(6)	476(2)	1(1)	HC(33)	69(2)	−84(5)	551(1)	0.5(8)
HC(34)	135(3)	−312(6)	553(2)	3(1)	HC(35)	186(4)	−374(10)	481(3)	7(2)
HC(36)	179(4)	−219(8)	404(3)	5(2)	HC(5)	10(4)	564(12)	374(3)	6(2)
HC(2.1)	−68(2)	279(6)	252(2)	1(1)	HC(2.2)	−110(3)	415(9)	258(3)	6(2)
HC(3.1)	−120(3)	100(8)	317(2)	4(2)	HC(3.2)	−170(3)	267(8)	326(3)	5(2)
HC(6.1)	−96(3)				HC(6.2)	−17(4)	844(10)	384(3)	8(2)
HC(7.1)	7(3)	654(8)	463(2)	4(2)	HC(7.2)				

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