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ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS CONTAINING AN ARSINE DONOR LIGAND

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CONTENTS

A. INTRODUCTION

Organometallic intramolecular-coordination compounds ($\overleftarrow{M-(C)_n-Y}$) (Y: donor ligand atom or group; $n \geq 1$) [1–6] can be classified into two groups; in the first, in which the cyclic ligand group has an M–C bond, a σ-coordination bond (M–Y σ-bond to the metal) is formed; in the second the cyclic ligand group forms a π-coordination bond (M–Y π-bond to the metal). Considering the first group, the σ-coordination compounds generally tend to form five-membered ring structures and the stability of the compounds is increased by the presence of electronegative atoms or by their replacement with more electronegative atoms in accordance with the five-membered ring structure theory [3].

$$A + B \rightarrow C \qquad (1)$$

In the cyclometallation reaction between A and B, this theory can conveniently be applied to judge whether or not this reaction is liable to proceed and product C is stable, and also whether C can form a five-membered ring. Where the donor ligand atom is oxygen or nitrogen, this tendency is especially strong, but, in the case of phosphorus or sulfur which have *d*-orbitals, it is rather less strong.

This review deals with organometallic intramolecular-coordination com-

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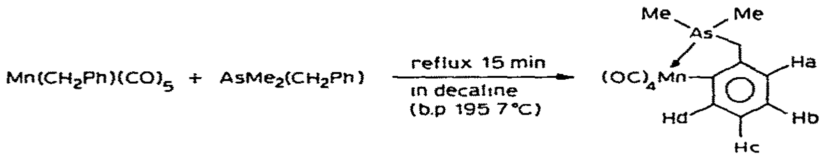
pounds containing an arsine donor ligand. The compounds have been referred to briefly in reviews concerning cyclometallated compounds by Dehand and Pfeffer [7], and Bruce [8], but no reviews specifically considering these compounds have yet been published.

The aim of this review is to show the structures, reactivities, properties and characters of organometallic intramolecular-coordination compounds containing an arsine donor ligand in comparison with those containing a phosphorus donor ligand [5]. The literature has been covered to 31 January 1981.

B. FIVE-MEMBERED RING COMPOUNDS

In the organometallic intramolecular-coordination compounds containing an arsine donor ligand, a five-membered ring structure is easily prepared by reaction between metal compounds and benzyl, tolyl, naphthyl, propyl compounds, or the like, similar to the preparation of organometallic intramolecular-coordination compounds containing a phosphorus donor ligand.



1

(2)

$-AsMe_2$: 1.56 ppm
$-CH_2AsMe_2$: 2.41 ..
Ha : 7.51 ..
Hd : 7.08 ..
Hb + Hc : 6.81 ..
Jab : 5.5 Hz
Jac : 3.5 ..
Jbd : 5.25 ..
in CS_2

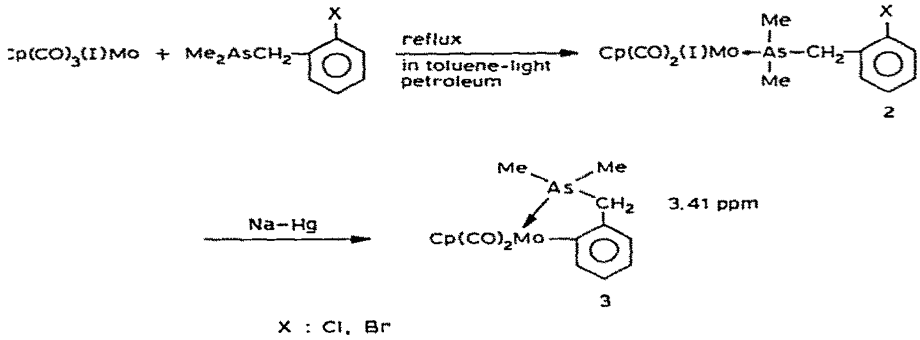
ν(CO) : 2067, 1989, 1978, 1953 cm^{-1}
in cyclohexane

As shown in eqn. (2) [9], benzylarsines react with manganese carbonyl similarly to benzylphosphine to afford the five-membered ring compound **1** by orthometallation; however, the benzylphosphine [5,9] more easily affords the compounds analogous to **1** in higher yield (61%) at lower temperature (in refluxing toluene, b.p. 110.6°C) [10]. Stone and co-workers [9] proposed the ring structure **1** on the basis that the IR spectrum contained the four ν(CO) bands expected for a *cis*-LL'Mn$(CO)_4$ complex and the proton NMR spectrum was consistent with the presence of the orthometallated ligand.

(*o*-Halobenzyl)dimethylarsine [11] reacts with tricarbonyl (η^5-cyclopentadienyl)iodomolybdenum under mild conditions to afford the intermolecular-coordination compound **2** having an arsine–molybdenum coordination bond. **2** is a stable intermediate of orthometallation, and further, reduction of **2** with sodium amalgam gives the orthometallation compound **3** similar to **1**. The orthometallation of amines, [3,12–15] such as benzylamines, proceeds very easily via very labile intermediates which are usually not capable of being isolated; however, in orthometallations with phosphines [5] or arsines, their reactivity is low and their reactions frequently proceed via very stable intermediates.

The reaction of (*o*-bromobenzyl)diorganoarsine [16] with n-butyllithium yields the corresponding (*o*-lithiobenzyl)diorganoarsines **4** by metal–halogen exchange. The compounds **4** are remarkably air- and moisture-sensitive and react with anhydrous chromic chloride to yield the metal exchanged compound **5** which is remarkably air-stable, but reacts with carbon dioxide to afford the (*o*-carboxylbenzyl)diorganoarsine **6**.

Tolylarsines also are less reactive than the corresponding phosphine compounds [17]; however, as shown in eqns. (5) and (6), tolylarsines yield intramolecular-coordination compounds **7** and **8** by a reaction similar to the tolylphosphines with metal halides [18]. The latter chloro-bridged compounds **8** easily react with pyridine, phosphine, arsine, silver acetate, silver benzoate, thallium acetylacetonate, or an excess of dimethylphenylphosphine to yield the corresponding bridge-ruptured compounds **9–12**. These reactions show the stability of the intramolecular-coordination bond in the compounds **8** because they proceed without fission of the metal–arsine bond.



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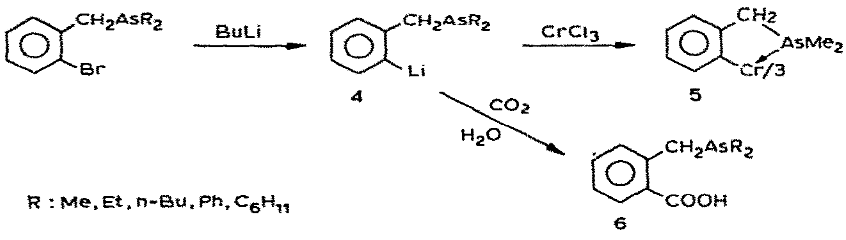

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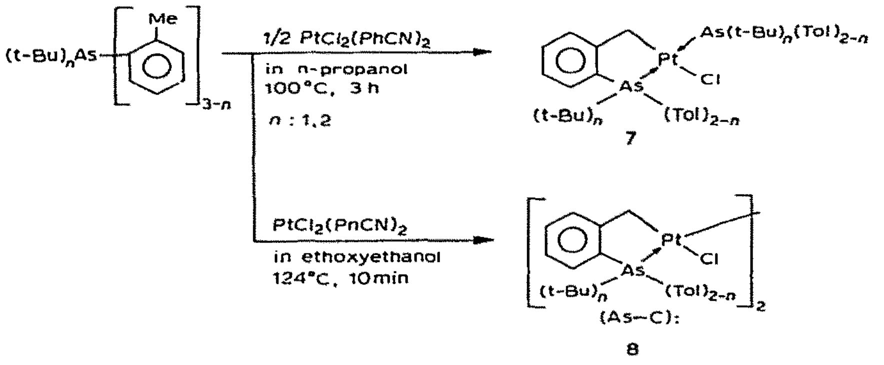

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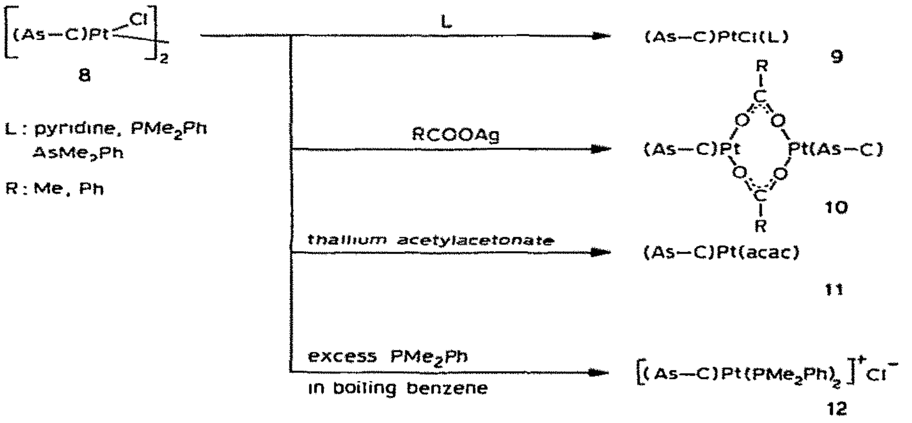


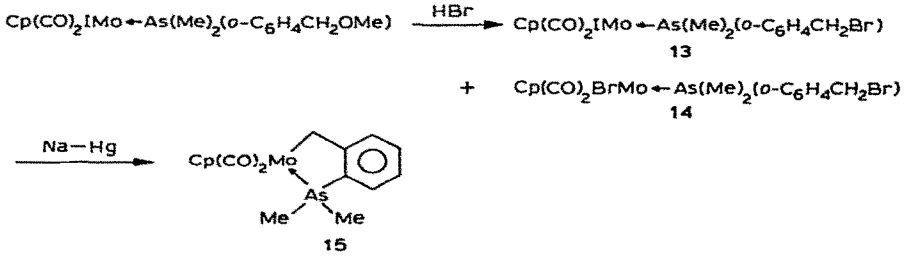
(7)

(8)

(9)

(10)

The intermolecular compound of [(*o*-methoxymethylphenyl)dimethylarsine] with dicarbonyl(η^5-cyclopentadienyl)iodomolybdenum was treated with aqueous hydrogen bromide to give the *o*-bromomethylphenyl compound **13** and its metal bromide **14** [11]. The mixture of **13** and **14** is reduced with sodium amalgam similarly to the reaction shown in eqn. (3) to afford the cyclometallated compound **15**. In the organometallic intramolecular-coordination compounds, two methylene protons or two group of methyl protons are frequently non-equivalent [11], the methyl protons in **15** resonate sharply at δ 1.41 and 1.39 ppm in the 90 MHz ^{1}H NMR spectrum and the benzylmethylene protons appear as a broad singlet at δ 2.88 ppm. The ^{13}C NMR spectrum of **15** in CDCl$_3$ at 25°C also shows two methyl resonances at 41.9 and 42.9 ppm.



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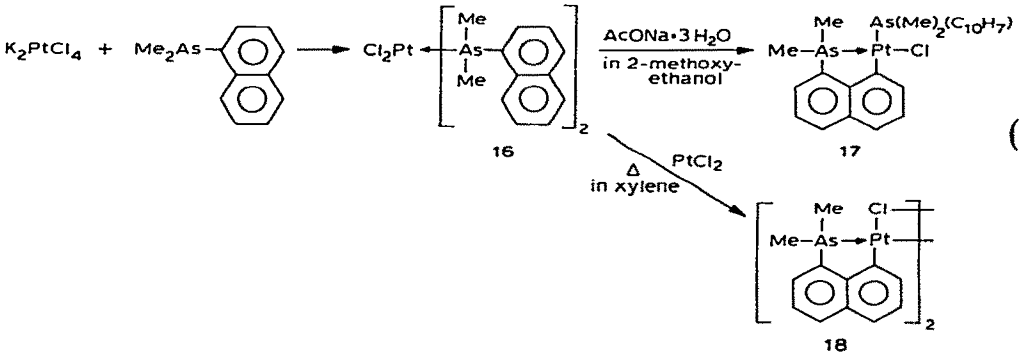

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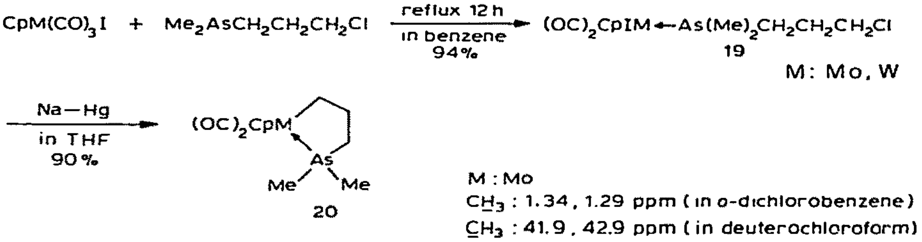

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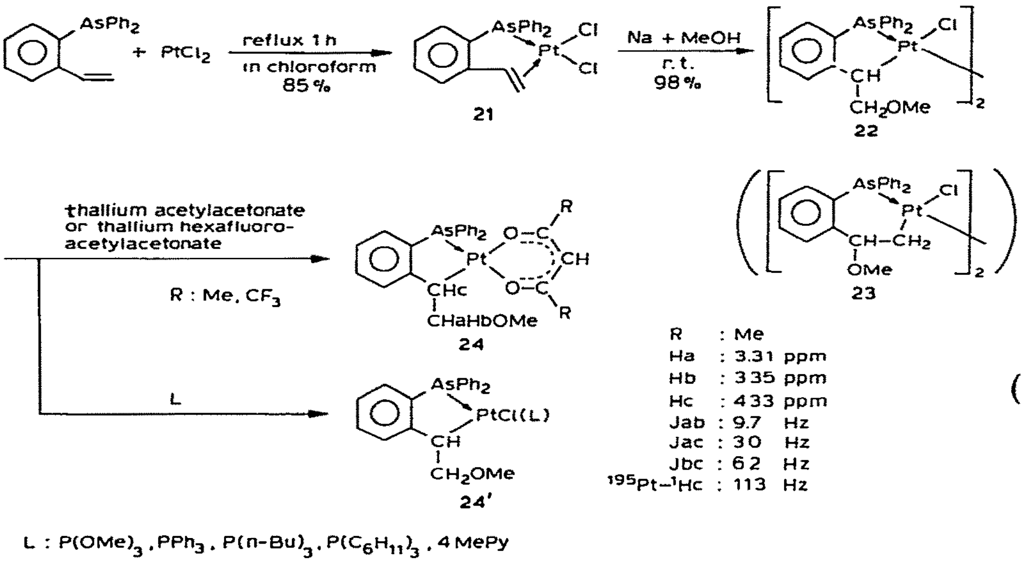


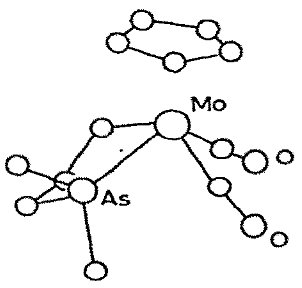
(14)

Dimethyl(1-naphthyl)arsine reacts with platinum halides in a manner similar to the corresponding phosphines to afford the intermolecular compound **16** having a coordination bond between the arsine atom and the platinum atom [19]. Further, on heating **16** in 2-methoxyethanol in the presence of sodium acetate, compound **17** cyclometallated at the *peri*-position is produced.

On the other hand, when the intermediate **16** was treated with platinous chloride the cyclometallated chloro-bridged compound **18** was produced. With neutral ligand such as pyridine, carbon monoxide, dimethyl-1-naphthylphosphine thallous acetylacetonate and silver acetate, **18** affords the corresponding ligand exchange compounds by reactions similar to eqns. (7)–(10).

In addition to benzylarsines, *o*-tolylarsines and 1-naphthylarsines, propylarsine also affords a five-membered ring compound by cyclometallation. For example, (3-chloropropyl)dimethylarsine reacted with tricarbonyl(η^5-cyclopentadienyl)iodomolybdenum to give the intermolecular complex **19** [11,20]. Cyclization was achieved in a few minutes by reduction with an excess of sodium amalgam giving the air-stable compound **20**. Similar cyclometallated tungsten compounds were also prepared [20]. The five-membered ring structure of molybdenum compound **20** has been determined from X-ray diffraction data by the heavy-atom method [21]. The molecular geometry is pseudo-square-pyramidal with a η^5-cyclopentadienyl ring occupying the position at the apex of the pyramid (Fig. 1).

The reaction of *o*-vinyldiphenylarsine with platinous chloride yields π-coordinated cyclometallation compounds **21** having a 5.5-membered ring [6,22]. Moreover the treatment of **21** with sodium methoxide affords a methoxide which has either a five- **22** or six-membered ring **23** [23]. To establish the structure of the methoxide, its chloro-bridge ruptured compounds **24** and **24′** were prepared by reaction with thallium acetylacetonate, thallium hexafluoroacetylacetonate, etc. Cooper and Guerney [22] presumed



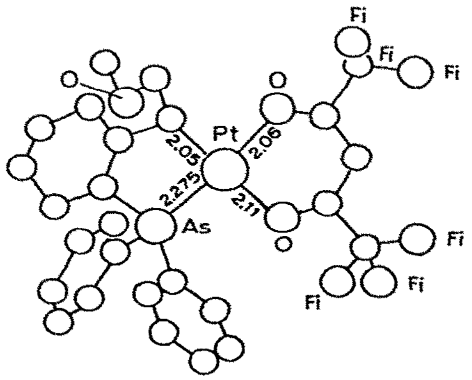


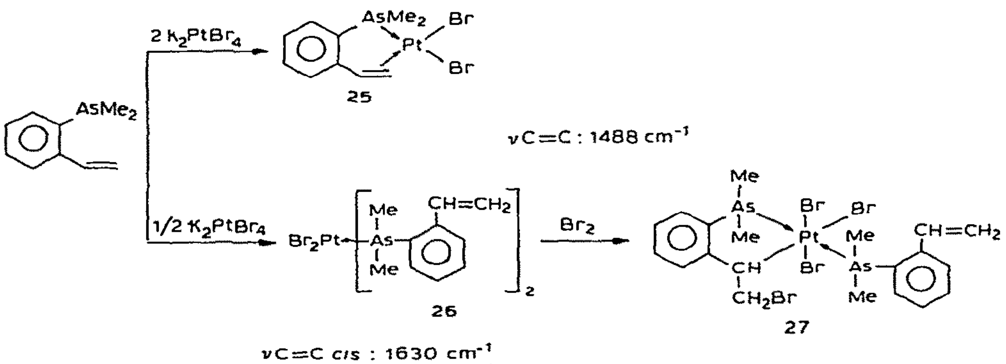
Fig. 1. The structure of dicarbonyl-η^5-cyclopentadienyl[(3-dimethylarsino)propyl]molybdenum, **20**.

Fig. 2. The structure of [1-(*o*-diphenylarsinephenyl)-2-methoxyethyl-As,C^1](hexafluoroacetylacetonato)platinum(II), **24**.

that the methoxy compounds have a five-membered ring structure by showing that the carbon atom bonded with a methyl proton is directly bonded with platinum because in hexafluoroacetylacetonate the methine quartet (Hc) is deshielded relative to that in acetylacetonate by 0.24 ppm and a value of 113 Hz for the $^{119}Pt-^{1}H$ coupling constant (120 Hz for hexafluoroacetylacetonate) is typical for a methine group σ-bonded to platinum in a cyclic system [24,25].

The five-membered chelate ring structure of **24** ($R = CF_3$) has also been determined by X-ray diffraction (Fig. 2) [26]. As the platinum–arsenic bond length (2.275 Å) is significantly shorter than the sum of the covalent radii (2.49 Å) for Pt and As, Cooper and Guerney [26] presumed a π-interaction between the atoms. Furthermore, considering the two Pt–O bonds from the potentially symmetrical hexafluoroacetylacetonato ligand, the bond *trans* to the σ-bonded carbon is only 0.05 Å longer than that *trans* to the arsine (cf. the difference of 0.104 Å between the Pt–O bond length *trans* to carbon and that *trans* to chlorine in $Pt(acac)Cl-CH(COCH_3)_2$) [27]. Hence, it is suggested that the tertiary arsine group in platinum(II) compounds shows a strong *trans* influence [28–32] similar to that caused by a carbon atom in the same position.

o-Styryldimethylarsine [33,34] reacts with a large excess of potassium tetrabromoplatinate to afford the intramolecular-π-coordination compound having the 5.5-membered ring **25** similar to **21**. On the other hand, upon reaction with a small amount of potassium tetrabromoplatinate, the excess of *o*-styryldimethylarsine prevents formation of an intramolecular-π-



(15)

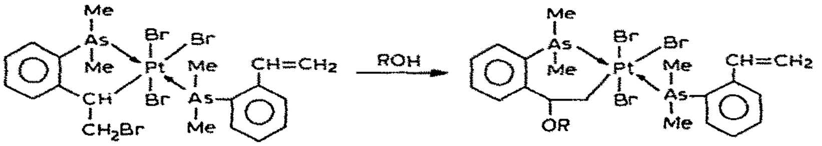
(16)

28 29

coordination bond because it acts as a new ligand in place of the olefin π-bond to platinum. A ligand exchange reaction or fission of the intramolecular-π-coordination bond proceeds with an excess of the arsine, to give the intermolecular-coordination compound **26**. Further, bromination of **26** affords the five-membered ring compound **27** which is similar to the alkoxide **22**. In 1967, Bennett et al. [33,34] could not definitely show whether the ring structure of the bromination product is five-membered **27** or six-membered such as the compounds **28** and **29**. In 1971, they determined the structure of the bromination product of a phosphine gold complex similar to **27** by single-crystal X-ray study [35], and presumed that the bromination product **27** of the arsine compound has a five-membered ring structure because its NMR spectrum shows resonance similar to that of the phosphine compound.

C. SIX-MEMBERED RING COMPOUNDS

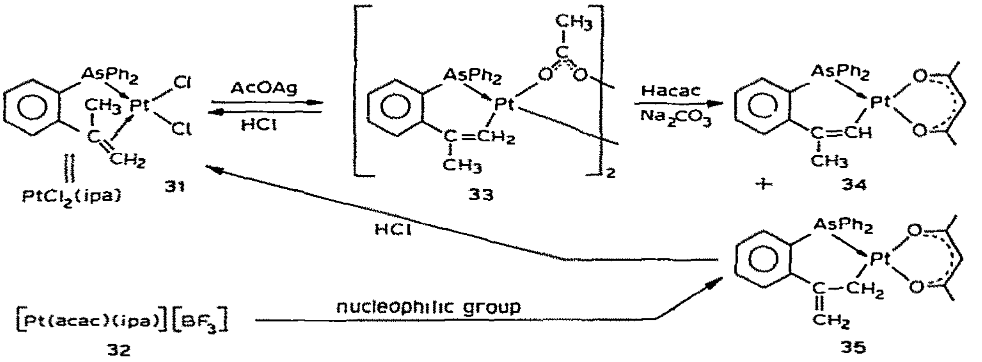
As shown in eqns. (14) and (16), if a reaction is considered to be able to give either a five- or six-membered ring, a five-membered ring usually results [1–5]. Six-membered ring compounds are usually produced either from reactions which do not have the possibility of producing a five-membered ring product, or as the derivatives of five-membered ring compounds. For example, on heating the five-membered ring compound **27** in methanol. ethanol or aqueous acetone, the six-membered ring compounds **30** are produced by ring expansion [36].



27 R : H, Me, Et 30 (17)

The structure of **30** ($R = Et$) has been determined by single-crystal X-ray study (Fig. 3) [36]. The ligands are arranged in a slightly distorted octahedron about the metal atom which is attached to the β-carbon atom of the side chain to give a six-membered chelate ring. The Pt–Br distances of mutually *trans* bromine atoms are equal, their value coinciding with the covalent radius sum. The Pt–Br distance *trans* to the σ-bonded carbon atom is significantly greater than the other two Pt–Br bond distances because of the *trans* influence weakening the Pt–Br bond due to the σ-inductive effect of carbon as a ligand atom operating in planar and octahedral complexes [28,31,32].

o-Isopropenyl(diphenyl)arsine platinum complexes **31**, **32** are treated with silver acetate, methoxide, triethylamine, etc., to afford the six-membered ring compounds **33**, **35** [37]. Both products are converted to the intramolecular-olefin π-complexes **31** by treating with hydrochloric acid. Treatment of the acetate-bridged compound **33** with acetylacetone and sodium carbonate affords a mixture of the desired products **34** and **35** via a stabilized carbonium ion [38,39] produced from the olefin double bond and platinum atom. In these products, the six-membered ring structure of the acetate-bridged dimeric compound **33** has been determined by X-ray analysis [37].



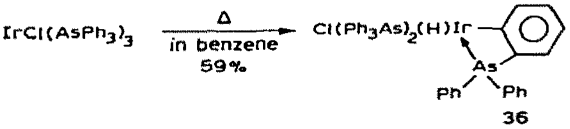
(18)

nucleophilic group : acetate, methoxide, hydroxide, triethyl amine

D. FOUR-MEMBERED RING COMPOUNDS

Four-membered ring compounds are capable of being prepared, usually only in the case of reactions which do not afford the five-membered ring compounds. Many four-membered ring compounds have been produced from phenylphosphine compounds [5] by orthometallation.

Phenylarsines also afford four-membered ring compounds by orthometallation, e.g., chlorotris(triphenylarsine)iridium(I) in benzene or cyclohexane at a reflux temperature as, in a reaction similar to the corresponding phosphines and stibine, shown in eqn. (19) [40]. Bennett and Milner [40] have shown by IR data (νIr–D and νIr–H) using deuterated phenylphosphine or deuterated solvent, that this orthometallation is a hydrogen abstraction reaction on the phenyl ring.



ν(Ir–H): 2170 cm⁻¹
ν(Ir–H): 805 cm⁻¹
ν(Ir–Cl): 257 cm⁻¹
Ir–H : −19.9 ppm

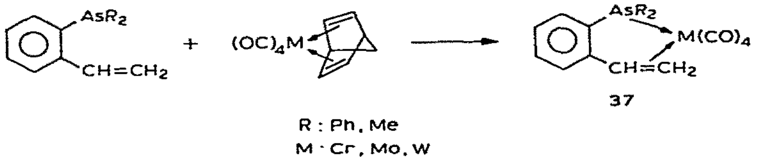
(19)

E. UNSATURATED COMPOUNDS

In organometallic intramolecular-coordination compounds, almost all compounds having a σ-coordinate bond from metal (M–Y σ-bond) to the ligand group containing an M–C bond, also have an M–C σ-bond. However, in organometallic intramolecular-coordination compounds containing a phosphorus donor ligand, the preparation of many compounds having an M–C π-bond has been reported, and the syntheses of similar arsine compounds comparable to the phosphorus compounds have also been published [5].

As described in eqns. (14), (15) and (18), the reaction between *o*-styryl- or isopropenylphenylarsine and platinum halide affords the 5.5-membered ring compounds **21**, **25** and **31**. The νC=C stretching vibration of these compounds shifts to ca. 1500 cm^{-1} with the coordination of the carbon–carbon double bond to platinum compared with the free νC=C which appears at 1620–1640 cm^{-1} (eqn. 15) [33]. X-ray analysis of **21** confirmed its intramolecular-π-coordination structure (Fig. 4) [26]. The olefin group makes an angle of 83.6° with the coordination plane and the olefin bond length is 1.44(3) Å, significantly longer than the 1.34 Å of uncoordinated ethylene. The arsine group exerts a strong *trans* influence (*trans* Pt–Cl bond length to arsine is 0.044 Å longer than that to the olefinic bond) [28–34].

The reactions of *o*-styryldiorganoarsines with norbornadienetetracarbonyl metal compounds **37** (metal = chromium, molybdenum and tungsten) also afford *o*-styrylarsine compounds having a 5.5-membered ring analogous to **21** and **25** [41].



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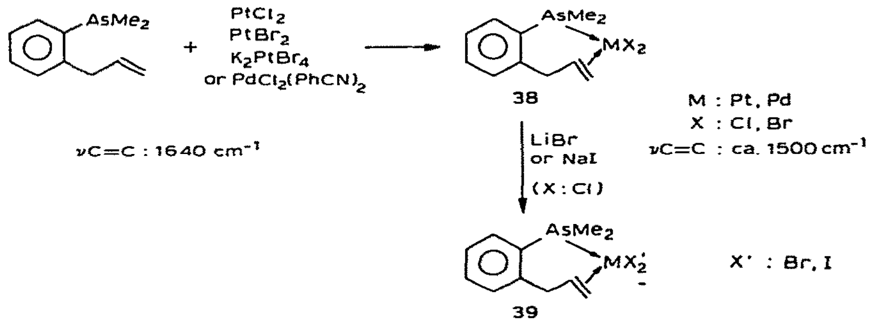

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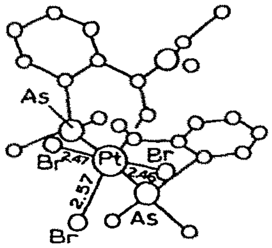


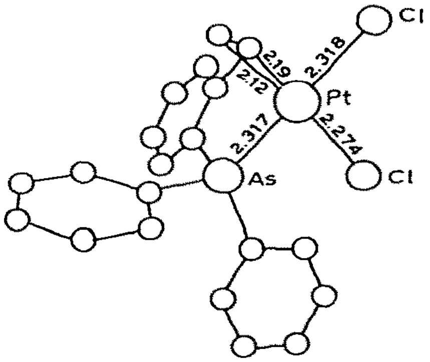


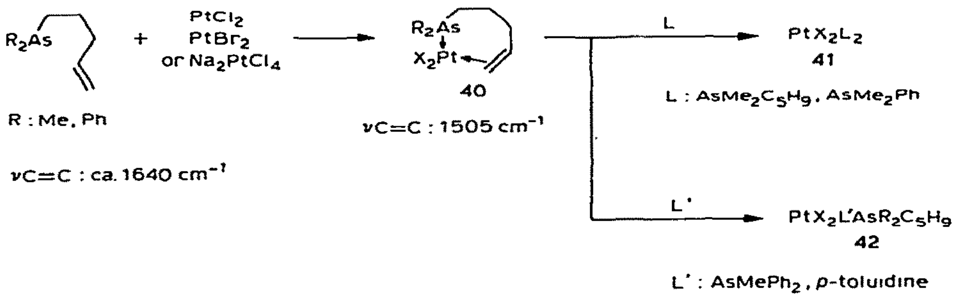
Fig. 3. The structure of **30** (R = Et).

Fig. 4. The structure of dichloro[diphenyl(*o*-vinylphenyl)arsine]platinum(II), **21**.

The terminal vinyl protons of these products show a large upfield shift of the vinyl proton resonances on coordination at 7.63–6.44 ppm compared with those of *o*-styryldiphenylarsine or *o*-styryldimethylarsine at 5.01–4.40 ppm.

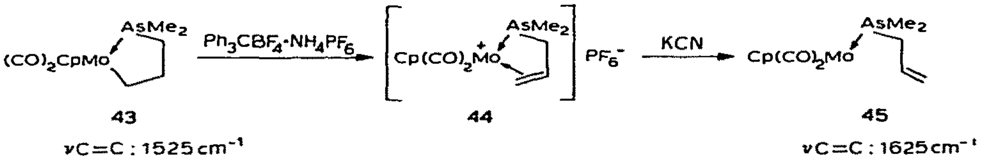
Generally, the 5.5-membered ring compounds have less strain and are more stable than the other olefin π-intramolecular-coordination compounds; however, 6.5- and 4.5-membered ring compounds have been also synthesized [6]. For example, *o*-allylphenyldimethylarsines react with metal halides to yield 6.5-membered ring compounds **38** as shown in eqn. (21) [33,34,42]. The bromides **39** (X = Br) are prepared directly from metal bromide or by reaction of chloride **38** (X = Cl) with lithium bromide, and the iodides are prepared by reaction of chloride with sodium iodide, although reaction of the palladium chloride derivative with sodium iodide gives only the iodide bridged compound [(*o*-allyldiphenylarsine)IPd—I]$_2$ (νC=C: 1640 cm^{-1}) by fission of the intramolecular-coordination bond. The corresponding phosphines form chelate compounds more readily than do the arsines; e.g. the phosphine palladium iodide can form a chelate complex (νC=C: 1508 cm^{-1}).

Pent-4-enyl compounds [43,44] also give 6.5-membered ring compounds **40** by reaction with metal halides and the corresponding bromides or iodides are also prepared from reaction of the chloride with lithium bromide or sodium iodide. However, these intramolecular-coordination bonds are not so strong, and the coordination double bond is readily displaced by other monodentate ligands such as tertiary arsine, *p*-toluidine and sodium thiocyanate.



(22)

Hydride-abstraction from the cyclic propylarsine molybdenum compound **43** with trityl tetrafluoroborate affords 4.5-membered ring compounds **44**. Further, **44** reacts with potassium cyanide to give isopropenylarsine by displacement of the unsaturated residue and not by the expected addition to the coordinated double bond.



(23)

F. CONCLUDING REMARKS

(i) Organometallic intramolecular-coordination compounds containing an arsine donor ligand form four, five and six, membered ring compounds and unsaturated compounds having a π-coordinate bond.

(ii) They prefer to form five-membered ring structures similar to the corresponding phosphine compounds.

(iii) They are generally more difficult to synthesize and more labile than the corresponding phosphine compounds.

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