GALLIUM AND INDIUM
ANNUAL SURVEY COVERING THE YEAR 1976

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Introduction, Reviews, and Books

Studies on organogallium and -indium chemistry during 1976 have remained at about the same level as those during 1975*; a modest amount of work on structure and bonding and studies on synthesis and reaction chemistry including one patent have been reported. This survey describes these topics in this order.

The reviews on 'Organometallic Compounds of Group III Elements (Al, Ga, In, and Tl)', one with an extensive bibliography [1] and the other with 105 references [2], and a book on 'Metal-to-Metal Bonded States of the Main Group Elements' which includes discussion of Al, Ga, In, and Tl compounds with references up to December 1973 [3] have been published.

Structure, Bonding, and Thermodynamics

Russian chemists determined the vapor pressures of R_3Ga (R= CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9), as well as $(C_2H_5)_2O$ and $(C_2H_5)_3As$, as a function of temperature using a null manometer. Heats and entropies of vaporization were calculated and compared with the previously published values [4].

One of the active interests in the chemistry of the Group III typical elements involves the question of the bonding of the cyclopentadienyl group (C_5H_5) to these metals. NMR Spectroscopy may, in principle, be an excellent tool for differentiating between the two extreme bonding types of C_5H_5: σ and π. Thus, Sergeyev has been able to classify about a dozen cyclopentadienyl derivatives from their ^{13}C chemical shifts as either σ- or π-bonded (Progress in Nucl. Magn. Resonance Spectroscopy, Vol. 9, Part 2 (1973) p. 112). Fischer et al., however, have mentioned in their NMR study on a series of $R_2MC_5H_5$ compounds (R= CH_3 or C_2H_5; M= Al, Ga, and In) that neither the ^{13}C chemical shift nor the primary C-H coupling constant may be used as a criterion for assigning a σ- or π-bonded structure to a given C_5H_5 compound [5]. A detailed analysis of the IR and Raman spectra of $(C_2H_5)_2MC_5H_5$ compounds (M= Al, Ga, and In) in both the solid and the liquid phases has ruled out a σ-bonded structure. The spectra of

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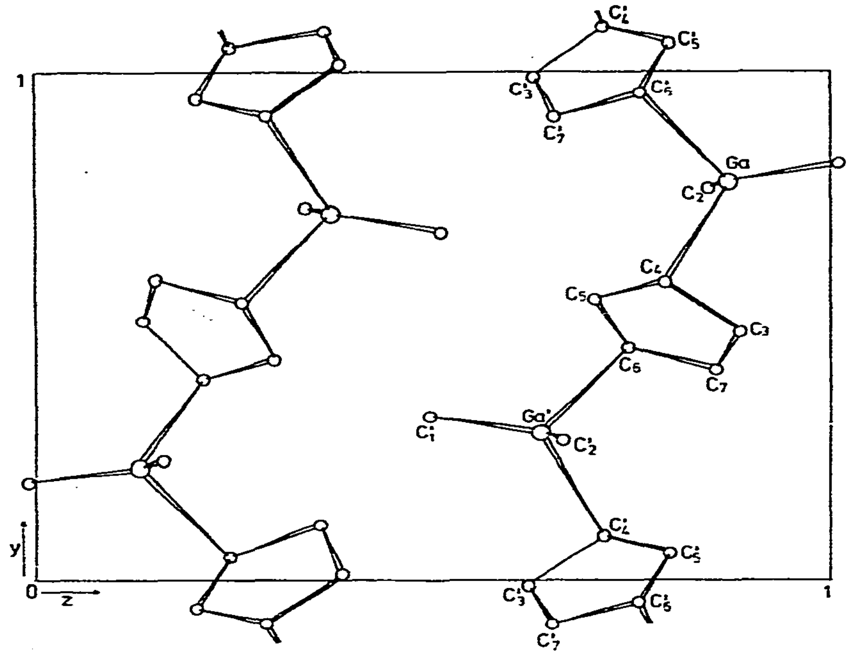
* R. Okawara, Gallium and Indium, Annual Survey Covering the Year 1975; J. Organometal. Chem., 130 (1977) 345.

liquid $(C_2H_5)_2GaC_5H_5$ and $(C_2H_5)_2AlC_5H_5$ show the presence of C_5H_5 rings with a symmetry somewhat lower than C_{5v}, while $(C_2H_5)_2AlC_5H_5 \cdot (C_2H_5)_2O$ has been established to involve pentahapto($\underline{h}^5$) C_5H_5–Al bonding [6]. Mertz et al. determined the crystal structure of $(CH_3)_2GaC_5H_5$ [7]. The structure consists of chains of the $(CH_3)_2Ga$ group bridged by the C_5H_5 rings. Each gallium atom has a distorted tetrahedral environment as shown in Fig. 1.

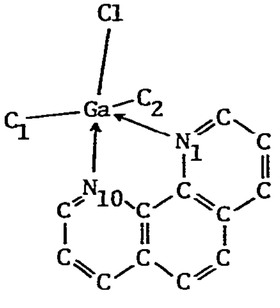


$Ga-C_1$	1.972(2) Å
$Ga-C_2$	1.962(1)
$Ga-C_4$	2.215(2)
$Ga-C_6'$	2.314(2)
C_1-Ga-C_2	127.0(2)°
C_4-Ga-C_6'	96.6(2)
C_4-Ga-C_1	105.8(2)
C_4-Ga-C_2	111.1(2)
$C_6'-Ga-C_1$	99.5(2)
$C_6'-Ga-C_2$	112.2(2)

Figure 1. Crystal structure of $(CH_3)_2GaC_5H_5$; projection on (011) (from ref. 7)

In an attempt to obtain insight into N–Ga and P–Ga donor-acceptor bonds, the structures of $(CH_3)_3Ga \cdot N(CH_3)_3$ and $(CH_3)_3Ga \cdot P(CH_3)_3$ were determined by electron diffraction in the gas phase [8]. The Ga–N bond (2.20 Å) was significantly longer than the sum of the covalent single-bond radii (Ga, 1.26 Å; N, 0.70 Å). The variation in the geometry of the free donor and acceptor on adduct formation also was discussed.

McPhail et al. studied the 1:1 complex of 1,10-phenanthroline (phen) and $(CH_3)_2GaCl$ [9]. The ^1H NMR spectra of the complex in dichloromethane, acetonitrile, and water are equally compatible with a four-coordinate ionic structure, $[(CH_3)_2Ga(phen)]^+$, a pseudo-rotating five-coordinate structure, and a symmetrical six-coordinate structure, <u>cis</u>-$[(CH_3)_2GaCl(phen)(solvent)]$. The former ionic species also has been suggested to exist not only from the infrared spectra (Nujol, KBr) which showed no Ga–Cl absorption in the 400–300 cm^{-1} range but also from the observed molecular weight of 166 (calcd. 315) in water. On the other hand, the latter two geometries are consistent with the molecular weights of 320 and 330 in acetonitrile and chloroform, respectively. An X-ray crystal structure analysis has resolved this ambiguity, confirming that $(CH_3)_2GaCl(phen)$ is a discrete, non-ionic, monomeric complex in the solid state. The gallium coordination geometry is that of a distorted trigonal bipyramid with two CH_3 groups and one of the phen nitrogen atoms defining the equatorial plane and axial sites occupied by the Cl atom and the other nitrogen atom of bidentate phen, as shown in 1 [9].



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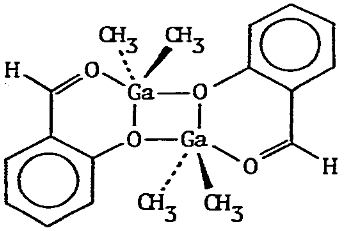
Ga-Cl	2.440(3) Å	$Cl-Ga-N_1$	91.2(2)°
$Ga-C_1$	1.956(9)	$Cl-Ga-N_{10}$	161.0(2)
$Ga-C_2$	1.952(10)	$Cl-Ga-C_1$	95.5(3)
$Ga-N_1$	2.119(6)	$Cl-Ga-C_2$	99.4(3)
$Ga-N_{10}$	2.433(6)	N_1-Ga-N_{10}	71.9(2)
		N_1-Ga-C_1	114.3(3)
		N_1-Ga-C_2	108.4(3)
		C_1-Ga-N_{10}	84.3(3)
		C_2-Ga-N_{10}	94.1(3)
		C_1-Ga-C_2	134.2(4)

A five-coordinate Ga atom was also demonstrated to exist by an X-ray structure analysis of salicylaldehydatodimethylgallium dimer, $[(CH_3)_2Ga\cdot C_7H_5O_2]_2$ [10]. As shown in 2, the structure consists of centrosymmetric dimeric units



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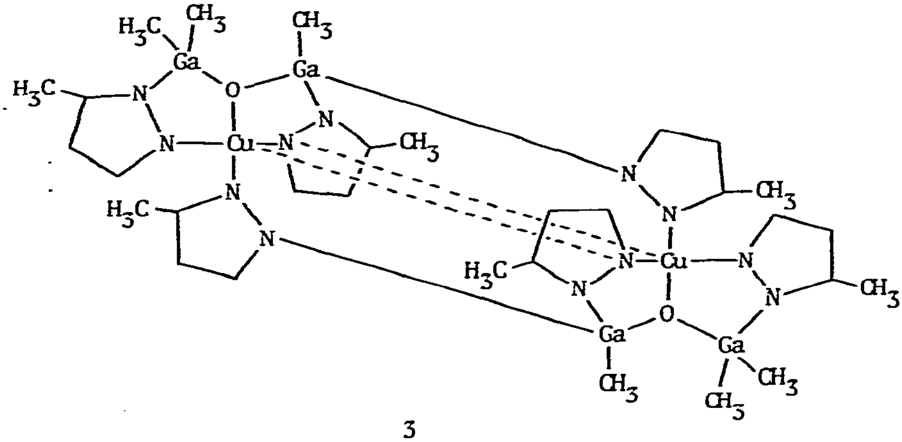
which contain five-coordinate gallium atoms having distorted trigonal bipyramidal geometry. The phenolic oxygen atom bridges the two Ga atoms and occupies an equatorial position on one Ga and an axial site on the other Ga atom. The remaining axial position on Ga is taken by the carbonyl oxygen atom while the two CH_3 groups occupy equatorial sites. The mass spectrum of the complex revealed as its strongest peak that due to the parent monomer ion minus one CH_3 group.

The sodium salt of dimethyl bis(3-methylpyrazolyl)gallate, $(CH_3)_2Ga(N_2C_4H_5)_2^-$, reacted with $CuBr_2$ in THF to yield a novel Cu(II) complex, $[(CH_3)_3Ga_2(N_2C_4H_5)_3CuO]_2$ [11]. An X-ray analysis showed that the centrosymmetric binuclear complex features copper atoms having distorted square-pyramidal geometry, bonded to four nitrogen atoms and one oxygen, as shown diagramatically in 3.



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This structure is the first example of a binuclear Cu(II) complex involving 'pyrazolylgallate' ligands. There is no major detectable intramolecular magnetic interaction between the two copper atoms (the distance between them is 3.383(1) Å) either directly or via the ligand system. The mass spectrum of the complex also was discussed.

X-Ray structural studies of tetramethylarsonium- and tetramethylstibonium-methyltrichloroindates, $(CH_3)_4M^+\cdot CH_3InCl_3^-$ (M= As, Sb) indicated that both the cation and the anion are tetrahedral, with the latter being distorted [12]. The tetrahedral cations and anions were found to form double-layers, as shown in Fig. 2.

Clusters of the type $\{[Mn(CO)_5]_2In(\eta-X)\}_2$ (X= Cl, Br, I), obtained by the oxidative insertion of In(I)X into the Mn-Mn bond of $Mn_2(CO)_{10}$, were characterized by osmometric, thermogravimetric, mass spectroscopic, IR, and Raman spectroscopic measurements. An X-ray structure analysis showed that these three clusters are isomorphous [13]. As depicted in 4, the molecules contain a planar four-membered In_2X_2 ring and have a center of symmetry. The plane defined by

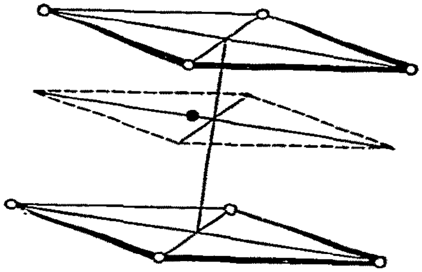
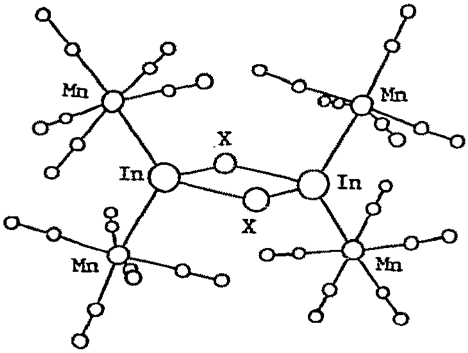


Figure 2. Section from the crystal lattice of $(CH_3)_4M^+ \cdot CH_3InCl_3^-$ (M= As, Sb); ○ In, ● As or Sb (from ref. 12)



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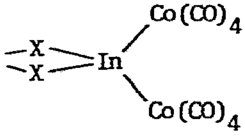
the four Mn atoms is perpendicular to the In_2X_2 plane. The average values of the In-Mn distance are 2.665(1) Å for X= Cl, 2.664(1) Å for X= Br, and 2.672(1) Å for X= I.

Interesting inferences about the σ- and π-bond character of metal-metal bonds can be extracted from pure nuclear quadrupole resonance (NQR) spectra, when either or both of the bonded metals have a non-zero value of their quadrupole moments. Thus, Brill et al. obtained the ^{59}Co, ^{115}In, ^{69}Ga, ^{71}Ga, ^{79}Br, ^{81}Br, and ^{35}Cl NQR parameters for four-coordinate In and Ga compounds containing metal-metal bonds; $XGa[Co(CO)_4]_2 \cdot THF$, $X_2GaCo(CO)_4 \cdot THF$, $(acac)BrGaCo(CO)_4$, $(acac)$-$Ga[Co(CO)_4]_2$, $\{XIn[Co(CO)_4]_2\}_n$, $XIn[Co(CO)_4]_2 \cdot THF$, $(acac)In[Co(CO)_4]_2$, $Ph_3PO \cdot In$-$[Co(CO)_4]_3$, and $Br_3In_3Co_4(CO)_{15}$ (X= Cl and Br, acac= acetylacetonate) [14]. The structures for some compounds are shown in 5-7. The sizable asymmetry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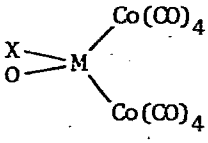
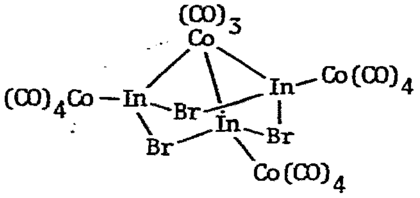

6: M= Ga, In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parameters (η) for ^{115}In (0.27-0.67) were taken to imply severe distorsion of the tetrahedral environment. The η(^{59}Co) values did not vary greatly (0.05-0.24) upon changing the groups bound to In and Ga, suggesting that π-bonding in the In-Co bond and Ga-Co bond is not a major factor in the compounds. The number of examples is limited but partial quadrupole splitting values for ligands derived from Sn(IV) Mössbauer spectra appeared to predict the trends in In(III) coupling constants.

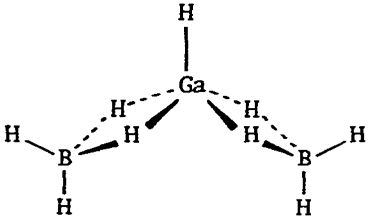
It has been possible to define individual ligand electric field gradient (EFG) contributions which, when combined appropriately, will approximate the EFG at a central atom. Recently, enough ^{115}In NQR data have become available to permit determination of partial ligand field gradients (PFG) at the In atom. Thus, Brill obtained the PFG values for ligands (CH_3^-, $C_2H_5^-$, $C_6H_5^-$, THF, Co-$(CO)_4^-$, Cl^-, Br^-, and CH_3COO^-) in a number of inorganic and organometallic In-(III) compounds to show that the additive EFG model may be applied to In(III) complexes along the same lines as have been applied to Sn(IV) [15].

Synthesis and Reaction Chemistry

Several reports of gallium tetrahydroborates, including $HGa(BH_4)_2$, exist (Progress in Inorg. Chem., 11 (1970) 99), but none of the reported compounds had been well characterized. Downs et al. [16] were successful in isolating HGa-$(BH_4)_2$ by reaction of powdered gallium trichloride with an excess of $LiBH_4$ at -45°C in the absence of a solvent (eq. 1), followed by careful fractionation *in vacuo*. The compound is a thermally unstable, volatile liquid (mp, ca. -70°C).

$$\frac{1}{2}Ga_2Cl_6 + 3LiBH_4 \longrightarrow GaB_2H_9 + 3LiCl + \frac{1}{2}B_2H_6 \qquad (1)$$

Both IR (vapor) and ^{1}H NMR (in $C_6D_5CD_3$ at 0°C) spectra are consistent with a structure possessing C_{2v} symmetry as shown in 8. This compound also was prepared in about 50% yield by reaction of $HGaCl_2$ with $LiBH_4$, again in the absence of a solvent at -45°C. Not only is the Ga compound extremely susceptible to



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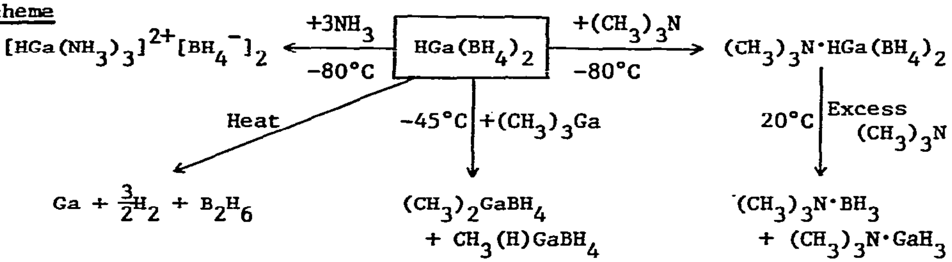
aerial oxidation and to hydrolysis, but it reacts with NH_3, $(CH_3)_3N$, and $(CH_3)_3$-Ga as indicated in the Scheme.

Scheme

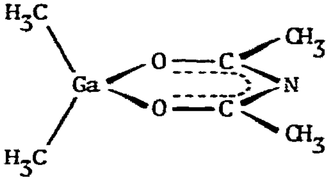


A Russian chemist prepared C_5H_5In and C_5H_5Tl by matrix condensation of In or Tl metal vapor with cyclopentadiene at 77°K [17]. Trimethylgallium, prepared by reaction of CH_3I with a Ga-Mg alloy, and $(CH_3)_3Ga{\cdot}O(C_2H_5)_2$, obtained from CH_3I and a Ga-Mg alloy in the presence of $(C_2H_5)_2O$, were purified by preparative gas-liquid chromatography using 10% silicone SE-30 on chromaton N-AW-HMDS, 0.25-2.35 mesh [18].

In order to gain some understanding of the nature of heterogeneous gas-solid reactions, the reaction of $(CH_3)_3Ga$ with AsH_3 in a static system between 203°C and 259°C was examined over the product surfaces which were $(CH_3)_{3-x}GaAsH_{3-x}$, where the average values of x were 1.1 and 2.2 at 203°C and 259°C, respectively [19]. The surface reaction (catalyzed by the product surface) forming $(CH_3)_2GaAsH_2$ occurred on the surface between adsorbed molecules of $(CH_3)_3Ga$ and AsH_3. The formation of GaAs via CH_4 elimination from $(CH_3)_2GaAsH_2$ or CH_3GaAsH was hindered by deposition of films of $(CH_3)_{3-x}GaAsH_{3-x}$ even at 420°C. The reaction mechanism has been suggested. The product-catalyzed reaction of $(CH_3)_3Ga$ with phosphine as well as arsine was described in a thesis [20]. Pyrolysis of organogallium compounds in the presence of arsine also was reported by Slepnev et al. [21].

Eberwein et al. reported the reactions of $(CH_3)_3Ga$ and $(CH_3)_5Sb$ with diacetamide, $HN(COCH_3)_2$, in pentane or toluene at 25°C or 100°C, giving dimethylgallium diacetamide (bp, 47-49°C/10 mmHg) and tetramethylantimony diacetamide (mp, 85°C) in high yields [22]. The complexes are monomeric in benzene or cyclohexane. Assignments of the IR, Raman, and ^1H NMR spectra of the Ga compound were described in terms of the molecule having C_{2v} symmetry shown in 9.

Trimethylphosphineimino-pentamethyldisiloxane and bis(trimethylphosphineimino)-dimethylsilane reacted with $(CH_3)_3M$ (M= Al, Ga, and In) to afford 1:1 adducts, 10 and 11, respectively [23], mp: 44-45°C, 26-27°C, and 20-21°C for M= Al, Ga, and In in 10, and 93-95°C, 80-82°C, and 84-86°C for M= Al, Ga, and In in 11, respectively. All these adducts were shown by cryoscopy to exist as monomers in benzene. Variable temperature ^1H NMR spectra in dichloromethane revealed that 11 exhibits non-rigid behavior near room temperature (eq. 2), while 10 are rigid adducts through coordination of the imino-nitrogen atom.



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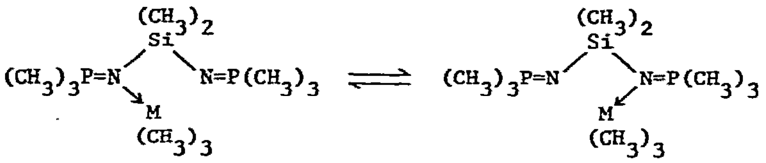
$(CH_3)_3P{=}N{-}Si(CH_3)_2{-}O{-}Si(CH_3)_3\cdot(CH_3)_3M$

10

$(CH_3)_3P{=}N{-}Si(CH_3)_2{-}N{=}P(CH_3)_3\cdot(CH_3)_3M$

11

An improved method for the preparation of alkyl-substituted gallium compounds by reaction of a Ga-Mg alloy with alkyl halides was described [24].



$$(CH_3)_3P{=}\underset{\downarrow}{N}{-}Si(CH_3)_2{-}N{=}P(CH_3)_3 \rightleftharpoons (CH_3)_3P{=}N{-}Si(CH_3)_2{-}\underset{\swarrow}{N}{=}P(CH_3)_3 \qquad (2)$$

$$\text{with } M(CH_3)_3 \text{ coordinated to the marked N}$$

References

1. J. P. Maher, Organometal. Chem., 4 (1975) 68.
2. B. H. Freeland and D. G. Tuck, Ann. Rep. Inorg. Gen. Synth., 3 (1974) 19; Chem. Abstr., 85 (1976) 33107y.
3. M. J. Taylor, "Metal-to-Metal Bonded States of the Main Group Elements," Academic Press (1975).

4. A. K. Baev, Yu. L. Gubar, S. E. Orekhova, and V. V. Zharov, Khim. Khim. Tekhnol. (Minsk), 10 (1976) 53; Chem. Abstr., 85 (1976) 182547u.
5. P. Fischer, J. Stadelhofer, and J. Weidlein, J. Organometal. Chem., 116 (1976) 65.
6. J. Stadelhofer, J. Weidlein, P. Fischer, and A. Haaland, J. Organometal. Chem., 116 (1976) 55.
7. K. Mertz, F. Zettler, H. D. Hausen, and J. Weidlein, J. Organometal. Chem., 122 (1976) 159.
8. L. M. Golubinskaya, A. V. Golubinskii, V. S. Mastryukov, L. V. Vilkov, and V. I. Bregadze, J. Organometal. Chem., 117 (1976) C4.
9. A. T. McPhail, R. W. Miller, C. G. Pitt, G. Gupta, and S. C. Srivastava, J. Chem. Soc., Dalton Trans., (1976) 1657.
10. S. J. Rettig, A. Storr, and J. Trotter, Can. J. Chem., 54 (1976) 1278.
11. R. T. Baker, S. J. Rettig, A. Storr, and J. Trotter, Can. J. Chem., 54 (1976) 343.
12. H. J. Guder, W. Schwarz, J. Weidlein, H. J. Widler, and H. D. Hausen, Z. Naturforsch., 31b (1976) 1185.
13. H. J. Haupt, W. Wolfes, and H. Preut, Inorg. Chem., 15 (1976) 2920.
14. T. B. Brill and D. C. Miller, Inorg. Chem., 15 (1976) 2553.
15. T. B. Brill, Inorg. Chem., 15 (1976) 2558.
16. A. J. Downs and P. D. P. Thomas, J. Chem. Soc., Chem. Commun., (1976) 825.
17. G. M. Kuz'yants, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1895; Chem. Abstr., 86 (1977) 5510b.
18. V. A. Fedorov and V. G. Makarenko, Tr. Khim. Khim. Tekhnol., (1975) 19; Chem. Abstr., 85 (1976) 143170w.
19. D. J. Schlyer and M. A. Ring, J. Organometal. Chem., 114 (1976) 9.
20. D. J. Schlyer, Thesis, Univ. California, San Diego (1976); Diss. Abstr. Int. B, 37 (1976) 1709; Chem. Abstr., 86 (1977) 22307h.
21. Yu. V. Slepnev, B. A. Salamatin, and L. A. Ivanyutin, Arsenid Galliya, (1974) 107. From Ref. Zh. Metall. (1975), Abstr. No. 11G564; Chem. Abstr., 84 (1976) 90203e.
22. B. Eberwein, F. Sille, and J. Weidlein, Z. Naturforsch., 31b (1976) 689.
23. W. Wolfsberger and H. Schmidbaur, J. Organometal. Chem., 122 (1976) 5.
24. L. M. Golubinskaya, V. I. Bregadze, B. I. Kozyrkin, and B. G. Gribov, U.S.S.R Patent 388,563 (1976); Chem. Abstr., 85 (1976) 5865a.