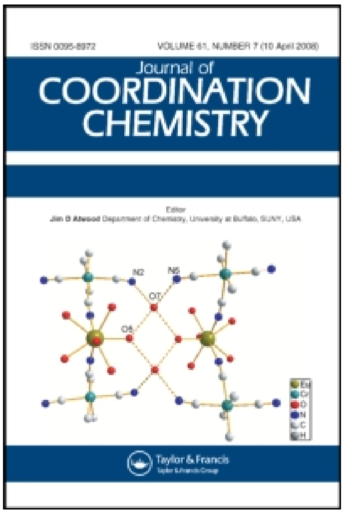

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CRYOSYNTHESIS OF COORDINATION AND ORGANOMETALLIC COMPOUNDS: HISTORY AND PRESENT STATE

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Review Article

CRYOSYNTHESIS OF COORDINATION AND ORGANOMETALLIC COMPOUNDS: HISTORY AND PRESENT STATE

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Interactions of metals with inorganic and organic ligands including polymers are reviewed. Direct methods of synthesis have many possibilities in comparison to conventional synthetic methods. However, cryosyntheses with chelate-forming ligands have not been sufficiently developed at the present time. Cryosynthesis is especially recommended for preparation of compounds difficult to obtain by traditional methods.

Keywords: Cryosynthesis; coordination and organometallic compounds; π-complexes; chelates

0. INTRODUCTION

The use of metal vapors in organic[1-4] and inorganic[4] chemistry led to the creation of a new area of synthetic coordination chemistry: the "direct synthesis" of metal complexes starting from metal vapors in the gas phase. In addition to hundreds of publications, a series of reviews[5-21] and monographs[22-27] have reported various aspects of this subject. In the majority of

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these publications only certain aspects were examined, shedding insufficient light on the overall role of direct metal-vapor synthesis in the modern chemistry of coordination and organometallic compounds. We hope that this paper elucidates such a role; the aim is metal-vapor syntheses (*i.e.* cryosynthesis) of the main types of coordination compounds, π-complexes and metal chelates. Indeed, as will be shown below, cryosyntheses have made a large contribution to the coordination chemistry of metal σ- and π-complexes, in particular, the metal-containing derivatives of olefins, alkynes, their cyclic counterparts, and (hetero)aromatic systems.

There is a difference between the metal vapor/cryosynthesis method and other types of direct synthesis[27] (oxidative dissolution of bulk metals, electro- and mechanosynthesis). For metal-vapor synthesis the bulk metal must be vaporized before its reaction with gaseous or frozen (in)organic ligand. This step is necessary to provide the metal in the absence of kinetic or thermodynamic barriers which accompany bulk metals, and is precisely the reason for success of cryosynthesis.

A gaseous atom of any element except the noble gases may be expected to be more reactive than the normal form of the element for two reasons.[5] First, the atom can react faster because it has minimal steric requirements and generally has readily available electrons or orbitals. Second, the atom is a species of higher energy than the normal state of the element (see the table of the heats of formation of the elements. Ref. 5).

Condensation of atoms in an isolated form on an inert surface at 77 K does not greatly change its energy with respect to room temperature, so the values $\Delta H_{298\,\mathrm{K}}$ can be used when considering the energetics of low temperature condensation reactions. The extra energy possessed by atoms compared with the normal states of the metals always causes some difference in behavior.[5]

Reactions between positive or even negative metal ions and (in)organic ligands have not been included in this review: this special area has been developing rapidly and is described in detail in several reviews.[28,29]

1. METHODS, CONDITIONS, EQUIPMENT, REAGENTS

Coordination compounds could be obtained by direct interaction of vaporized atomic metals and ligands in the gas phase.[1–3,22,30–32] However, the scope of this approach is strongly limited by instability of complexes at high temperatures, which frequently leads to breakdown of coordination compounds and/or transformation of ligands. The highest efficiency in gas-phase syntheses is reached by co-condensation of metal vapors and ligands at low temperature "cryosynthesis".[5–8,18,22,23]

The working temperatures usually range from 10 to 273 K, although in some cases higher (295–325 K),[33–35] and lower (for example, liquid helium)[36] temperatures are used. The cryoscopic effect is examined in some reviews[7,17,18] and a monograph.[23] It is emphasized[18] that cryosynthesis using metal vapors is essentially irreversible due to experimental conditions. The metal vapor, obtained at high temperatures (2000–2500 K) in equilibrium with the condensed phase, is transported in vacuum as a flow (current) of atoms, reacting at low temperature with the condensed phase of ligand or its precursor (in the "matrix" of the ligand).

In order to evaluate the extent of isolation of metal atoms in the matrix of (in)organic substance, it is possible to use the proportion M/R, where M and R are the amount of atoms (or molecules) of the substance matrix and of the metal atoms in this matrix, respectively. For a matrix which is inert to metal,[37] a good isolation of atomic metals is reached when $M/R > 300$. The magnitudes $M/R = 6$–100 are usually used in cryosynthesis, since, evidently, a large amount of (in)organic substance is not necessary to interact with metal atoms.

The matrix becomes more "rigid" with high cooling of the reaction chamber's walls (till liquid helium temperature) and diffusion of atoms and their aggregation is hindered. Moreover, at 4 K it is possible to observe spectroscopically the formation of compounds which are unstable at liquid nitrogen temperature.

Equipment for direct synthesis of metal complexes in the gas phase is described in a series of papers;[7,12,25,38–40] the design is not complicated with high-vacuum techniques. The types of apparatus are different by the methods of metal evaporation used and the introduction of the ligand into the reaction chamber.

Metal vaporization is carried out by resistive heating, induction heating, bombardment with electrons of a few kV, cathodic sputtering, and vaporization using lasers.[5,22,41] The technological breakthroughs in metal vaporization make it possible to use almost all metals of the Periodic Table,[5,7,13,22] in particular, such refractory ones, as niobium, molybdenum and tungsten.[2,3,7,13,15,32,42,43] The advantages and disadvantages of these methods of vaporization are examined,[6,7,41] as well as the ways to introduce the ligand into the reaction chamber and to isolate the coordination compounds formed in the cryosynthesis reactions. Table I (borrowed from the review 7) contains information about the vaporization temperatures of some metals in vacuum. The temperatures given are those at which the metal has a vapor

TABLE I Evaporation temperatures of metals in vacuum[7]

T°C < 1000	1000–1400	1400–1700	1700–2000	2000–2500	> 2500
Li	Be				
Na, Mg	Mn, Cu	Cr, Fe, Co	Ti, V		
		Ni			
K, Ca, Zn	Ag, Sn	Pd		Zr, Ru, Rh	Nb, Mo
Pb, Cr, Cd	Au		U	Pt	Hf, Ta
	Pr, Nd, Gd, Tb	La, Ce, Lu			W, Re
Sm, Eu	Dy, Ho, Er, Tm				Os, Ir

pressure of 0.01–0.1 Torr, sufficient to give rapid evaporation under high vacuum.[7]

Various organic and inorganic ligands are used in cryosynthesis, mainly unsaturated aliphatic, aromatic and heteroaromatic hydrocarbons and their funtionalized derivatives, dinitrogen, dioxygen, carbon and nitrogen oxides, *etc.* The maximum possible number of electrons which the ligand can donate to metal distinguishes, unsaturated hydrocarbons, monoolefins,[22,33–36] diolefins,[13,22,41,44–46] cyclic dienes[22,33–36,47–50] and trienes.[50]

Acetylene and its substituted derivatives have also been used as ligands, although less commonly.[5,13,14,22,33,46] The most widely used ligands in cryosynthesis of metal complexes are the aromatic compounds (especially benzene and its derivatives);[5,12,42,43,51–56] heteroaromatic ligand systems including thiophene,[18] pyridine and its derivatives[7,16,22,57] and α,α'-bipyridine.[58]

In addition, oxygen-containing organic derivatives are also used: ethers,[22] ketones (in particular, acetone),[45,59] β-diketones,[60] organic acids,[16] their anhydrides[16] and acyl halides,[13] as well as inorganic compounds.[7,15]

The transformations which take place during cryosynthesis of metal complexes are of two types: reactions of σ- and π-coordination of metal atoms and reactions of insertion of metals into a C–X bond (X = H, Hal). The first type of reactions leads, mainly, to π-complexes. The second category includes the insertion of a metal into C–H[15,18] or C–Hal[15,22,30,61] bonds and the formation of organometallic compounds with σ-metal–carbon bonds.

2. SYNTHESIS OF METAL COMPLEXES WITH SIMPLE INORGANIC LIGANDS

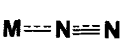
Timms[3] used phosphorus trifluoride as a ligand in one of his first pioneering works devoted to cryosynthesis; the reactions can be presented as follows (1):

$$M + nPF_3 \rightarrow \underset{\mathrm{I}}{M(PF_3)_n} \tag{1}$$

where $M = Ni$, $n = 4$; $M = Fe$, $n = 5$; $M = Cr$, $n = 6$. The binuclear complex $Co_2(PF_3)_8$ was also obtained. The same ligand has been used to synthesize other trifluorophosphine complexes.[62] All products were isolated at 77 K having yields of 25% (Fe), 50% (Co), 65% (Cr), 70% (Pd) and 100% (Ni).

The group PF_2 has a bridging function in the bridged binuclear complexes of cobalt[3] and iron.[63] Complexes of other phosphine ligands have been obtained under the same synthetic conditions,[63] for example $M(PMe_3)_n$, $M = Co, Ni, Pd$, $n = 4$; $M = Fe$, $n = 5$. The mixed-halide nickel complex of difluoromonochlorophosphine $Ni(PF_2Cl)_4$ was described in the same paper.[63] Preparation of an analogous complex of phosphine itself was unsuccessful, however, the mixed-ligand complex $Ni(PH_3)_2(PF_3)_2$ was isolated; it can be transformed to $Ni(PF_3)_4$ at 273 K.[61]

In many cases cryosynthesis has been used to obtain complexes of homo- and heteronuclear diatomic molecules. Thus, *mono-* and *bis*(dinitrogen)platinum(0) complexes were prepared by co-condensation of platinum vapors with N_2 molecules at 4.2–10 K in solid argon, while the reaction in solid nitrogen leads to tri- or dinitrogenplatinum(0).[64] These compounds were characterized by IR-spectroscopy, as was the titanium complex $Ti(N_2)_6$, obtained by co-condensation of atomic titanium with N_2 at 10–15 K.[65] In general, the structures of metal–dinitrogen complexes could be represented as follows:[66]


II

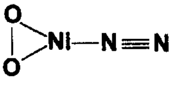

III


IV

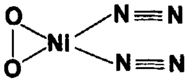

V

The majority of dinitrogen complexes have the metal in the lowest oxidation state, and back-bonding, though weak, is important for stabilizing the complexes.[66]

EPR, FTIR and UV/visible spectroscopy (experimental and calculated) have been used to characterize binary dioxygen complexes of nickel, palladium and platinum $M(O_2)$ and $M(O_2)_2$ in low-temperature matrices, synthesized by co-condensation of metal vapors with molecular oxygen at 4.2–10 K.[67] The mixed-ligand complexes, $(O_2)M(N_2)_n$, where $M = Ni, Pd$, Pt, were obtained in an argon matrix at 6–10 K.[68] These compounds have different compositions and structures. For example, the formulae **VI** and **VII** are assigned to $(O_2)Ni(N_2)$ and $(O_2)Ni(N_2)_2$, respectively, on the basis of the spectroscopic data.



VI



VII

Bidentate coordination of O_2, as well as monodentate coordination of N_2, corresponds to general ideas about the coordination of homodiatomic molecules.[69]

A large series of publications (among them Refs. 70–73) is devoted to interaction of metal atoms with carbon monoxide. These reactions are usually conducted in a rotating cryostat which is simply a stainless steel drum, containing liquid nitrogen and rotating ($\sim$2400 rpm) under high vacuum (less than 10^{-5} Torr). Vapors of both metal and substrate are directed onto the outer surface of the rotating drum from opposite sides.[74]

Cu atoms react with CO in a rotating cryostat at 77 K, forming CuCO and $Cu(CO)_3$, which have been identified by EPR spectroscopy.[72] CuCO is unstable and disappears rapidly above 77 K; paramagnetic $Cu(CO)_3$ is significantly more stable. In addition to these mononuclear carbonyls, the diamagnetic dinuclear carbonyl $Cu_2(CO)_6$ is formed in significant yields in adamantane and cyclohexane matrices at 77 K, indicating mobility of copper atoms on the solid hydrocarbon surface. This species is most likely produced by reaction of $Cu(CO)_3$ with a mobile copper atom followed by further reaction with CO (2), rather than dimerization of $Cu(CO)_3$ (3):[33]

$$Cu(CO)_3 + Cu \rightarrow Cu_2(CO)_3 \xrightarrow{CO} Cu_2(CO)_6 \tag{2}$$

$$2Cu(CO)_3 \rightarrow Cu_2(CO)_6 \tag{3}$$

A series of metal carbonyls $M(CO)_n$, where M = Co, Mn, Cr, Fe, Ni, Pd, Pt, Rh, Cu, Ag, Ir, Eu, and Nd, have been obtained in argon (or nitrogen,[75] M = Cu) matrices (21 and references therein) and studied by UV/visible spectroscopy. The synthesis of aluminium carbonyl $Al_x(CO)_2$[16] is especially interesting, because it shows the possibility to synthesize complexes of non-transition metals, in addition to compounds of transition metals and lanthanides. The application of Raman spectroscopy has allowed characterization in an argon matrix (4.2–10 K) of the binary complexes $Ni(N_2)_m(CO)_{4-m}$, where $m = 1$ or 3, by co-condensation of nickel vapor, nitrogen and carbon monoxide.[76]

The accepted model for bonding between CO and a metal is σ-donation of the p electrons of the C to the metal orbitals with simultaneous π back-bonding of the metal d electrons to the unoccupied π anti-bonding orbitals of CO.[77] The structures of metal carbonyls can be explained using the 18-electron rule;[38,66] Cr, Fe and Ni bind six, five and four CO ligands, respectively, to give monomeric compounds. The carbonyls of Mn and Co form metal–metal bonded dimers to attain an 18-valent electron configuration. The paramagnetic 17-valent electron complex $V(CO)_6$ is an exception: in order to achieve an electron count of 18, it would have to dimerize to give a 7-coordinate species; such an arrangement is however sterically unfavorable.[66] The various structures of metal carbonyls (and isocarbonyls) are presented in,[66] as well as a MMO description of the metal–CO binding in them. It is emphasized that CO acts as a strong "π-acid", forming the products where "back-bonding" takes place, stabilizing the M–CO bond. In multinuclear complexes CO can adopt doubly and triply bridging coordination modes, recognizable in neutral carbonyl complexes by characteristic ν(CO) frequencies.[66] The most recent data on metal carbonyls are presented in a review.[78]

The well-known nickel tetracarbonyl, obtained more than 100 years ago by reaction between bulk metal and CO, could also be synthesized by the unusual direct interaction (4) between nickel gas and CO_2 (as well as with CO) with a yield of $\sim 10\%$:[5]

$$Ni + CO_2 \rightarrow Ni(CO)_4 + NiO + CO \qquad (4)$$

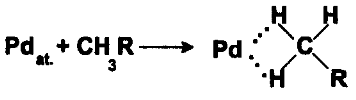
In addition to the above diatomic molecules, carbon monosulfide can also react with transition metals; formation of $Ni(CS)_4$ was shown by IR and mass spectroscopy.[79]

Attempts to induce nitrogen monoxide to react with metals were made; however, in this case only stable mixed-ligand complexes $Co(NO)(PF_3)_2$ and $Mn(NO)_3(PF_3)_3$[5] have been obtained. The latter is transformed to $Mn(NO)_3CO$ quantitatively in a CO atmosphere (1 atm, 293 K). Interaction of iron vapors with NO in argon at room temperature[45] is accompanied by the formation of the complex Fe(NO) with unknown structure.

Carbon disulfide has also been used in cryosynthesis: the complexes $Ni(CS_2)_n$, where $n = 1, 3$, were obtained and examined by UV-spectroscopy.[80] Synthesis of metal complexes with other di- and triatomic molecules using matrix isolation conditions have been reported;[81–88] A FT-IR and *quasi*relativistic density functional theory investigation of the reaction products of laser-ablated uranium atoms with NO, NO_2 and N_2O was described.[81] The reaction kinetics of chromium atoms with simple molecules, such as HCl, N_2O, Cl_2, and O_2, were presented.[89]

In the case of ammonia, along with the adduct $FeNH_3$,[45] the formation of an insertion product into the N–H bond was reported; perhaps this compound has the formula $HNiNH_2$.[25,90] A similar transformation, observed for water, leads to the product HNiOH.[25,91] The cryosynthesis of the complex of iron with methylaminodifluorophosphine $[CH_3N(PF_2)_2]_4Fe$ allowed the structure to be established by X-ray diffraction.[92] It is interesting that iron is penta-coordinate with three monodentate N-donor methylaminodifluorophosphine ligands and one molecule that acts as a bidentate P,N-donor ligand.

Formation of stable palladium adducts with alkanes (5) is emphasized; the structure **VIII** of a donor–acceptor π-complex, which differs from usual π-complexes, is assigned to these adducts.[34] Additionally, a recent review[93] is devoted to the activation of C–H bonds in alkanes by free metal atoms and metal clusters, as well as to the topics on σ-coordinated dihydrogen and σ-coordinated silanes.



VIII

(5)

Thus, in spite of the fact that simple organic molecules were used as ligands for cryosynthesis as far back as 30 years ago,[1–6] significant interest continues for cryosynthetic procedures.[75,78,81–89]

Table II summarizes the syntheses of metal complexes with simple inorganic molecules starting from metal vapors.

3. CRYOSYNTHESIS OF π AND σ METAL COMPLEXES

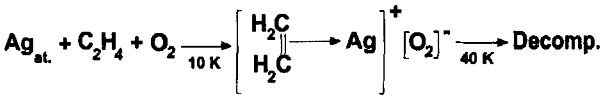
a. Interaction of Metals and Olefins

The simplest π-complex compounds (6) are obtained by interaction of metal vapors with alkenes (mono-olefins). Co-condensation of silver vapors and

TABLE II Cryosynthesis of metal complexes with simple molecules

Metal	*Ligand*	*Product*	*T*, K	*Yield*, %	*Ref.*
Ni,Pd,Ag,Pt,Rh_n $n=1-3$	O_2	$M_m(O_2)_l$ $m=1-4$, $l=1, 2, 4, 6, 8, 12$	4,2–77	5–15	67,94–96
Cr, Fe, Co, Ni, Pd	PF_3	$M_n(PF_3)_m$ $n=1, 2; m=3-8$	77	25–85	63,97
Fe	PF_3	$(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$	77	25	63,97
Ni	$PClF_2$	$Ni(PF_2Cl)_4$	77	32	63,97
Ni, Mn	PF_3+X $X=PH_3$, NO $(n=2, 3; m=1, 2)$	$Ni(PF_3)_nx_m$	77	10–15	63,97
Pt, V, Ti, Pd	N_2	$M(N_2)_n$, $n=1, 3, 6, 12$	4–15		6,63,64,98,99
Ni, Ti, Ag, Rh, Ir, V, Al, Cu, *etc.*	CO	$M_n(CO)_m$ $n=1-4; m=1-12$	4–77		5,16,65,71–73, 76,77,100–106
Ni, Pd, Ag, Pt, Au, Co	O_2+X $X=N_2$, CO	$(O_2)M(X)_{1-4}$	6–12	6–40	68,107–109
Ni	$CO+N_2/Ar$	$Ni(CO)_n(N_2)_m$ $n, m=1-3$	4,2–10		100
Ni	CS_2	$Ni(CS_2)_n$, $n=1,3$	10–12		80
Ag	SiO	$Ag(SiO)_{1-3,n}$	77		110
Cr	$P(OMe)_3$	$Cr\{P(OMe)_3\}_6$	77		6
Cu	CH_4	$HCuCH_3 \rightarrow CuCH_3$, CuH	12		111
Li	CCl_4, C_2Cl_6	Li_4C, Li_6C_2	1073–1273		112
Ag	CO_2	$Ag(CO_2)$	10–25		113
Cr, Mo, Co, Ni, Ag, Au, Fe, Cu, Pd	Molten salts $\{KNO_3$- $LiNO_{2-3}$; (K,Na,Li)OAc; KNCS$\}$	Metal oxides or metal powders	413–443		114

ethylene in the presence of dioxygen at 10 K leads to the unstable ethylene–silver complex **IX**, which decomposes at 40 K:



(6)

IX

The ethylene complexes of cobalt (in argon, 12–15 K[115]), nickel (in argon, 10–77 K;[116] in helium[36]), palladium (in helium, 300 ± 5 K, 0.5–0.8 Torr[34]), and copper (in argon, 295 and 395 K, 500–600 Torr[33]) have been described. The gas-phase kinetics of reactions of neutral transition metal atoms with olefins (ethylene, propene, butene and *i*-butene)[35] were studied for direct interaction between yttrium, molybdenum, zirconium, and niobium with alkenes.

A series of platinum π-complexes with propene and butene, as well as with allene,[117] has been obtained at 77 K. The effective rate constants of these reactions were determined under helium pressure (0.5–0.8 Torr) at 300 K; it was shown that under similar conditions Y, Zr and Nb interact rapidly with alkenes while Mo reacts slowly.[35] Kinetic data, for interaction of mono-olefins (ethylene, propylene, 1-butene, 0.5–0.8 Torr) with transition 3*d*- and 4*d*-metals (Sc, Ti, V, Ni, *etc.*), have been reported.[34,36,45]

The 1 : 1 adducts are formed[45] by interaction of ethylene with iron, while copper forms the complex $Cu(C_2H_4)_2$.[33] Interaction of gallium atoms[118] with ethylene in adamantane on a rotating cryostat at 77 K gave the cyclic σ-bonded gallacyclopentane **X**:

X

There are no X-ray diffraction data on metal complexes with olefins obtained by cryosynthesis; however, the ideas[35] and the proposed scheme of a donor–acceptor model of the metal–alkene bond (Figure 1)[38] are useful for understanding the coordination of a metal in olefin complexes. The ligand donates π electron density to a metal orbital of σ symmetry directed to the center of the ligand π system, and the metal in turn back-bonds

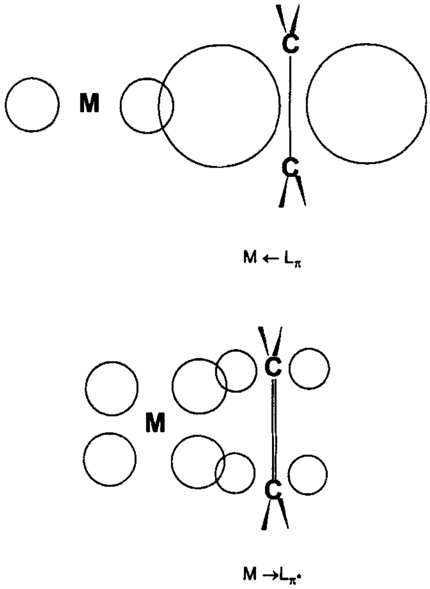
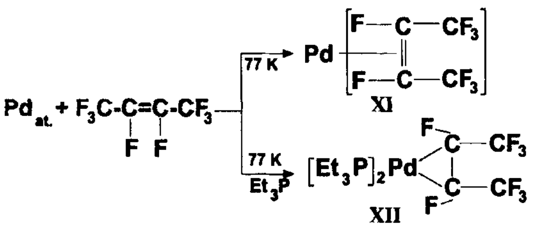


FIGURE 1 Bonding in metal–olefin complexes.

electron density into a ligand π^* orbital. The result is a synergism that, as in the case of the metal carbonyls, leads to relatively strong bonding.[38] Even in this simple form it is clear that such bonding can occur effectively only with a low valent metal (*i.e.*, oxidation states –1 to +2) with populated π symmetry orbitals (*i.e.*, a metal late in the transition series).

In the example of the Al–C_2H_4 complex, the structure could be explained using Density Functional Theory (DFT) and Topological Method (ELF).[119] It is shown that this complex has a C_{2v} structure and a $^2B_2$ ground electronic state with a strong bond (–13.3 kcal/mol compared to experimental value of –16 kcal/mol), the Al–ethylene bonding is mostly electrostatic.[119] A theoretical study of the reaction of copper dimer with ethylene using SCF/CASSCF/MP2 methods has been described.[120] The studies revealed that the perpendicular approach of Cu_2 is more favored than parallel. The strong bonding is assisted through donation of π-electron density from ethylene to a 4*p* orbital of Cu.

In addition to metal–alkene reactions in the cryosynthesis conditions, the interaction of transition metals and halogen-substituted unsaturated hydrocarbons also leads to π-complexes. Thus, atomic palladium, reacting with *cis*-perfluorobutene (7) at 77 K, forms the coordination compound **XI**:[22]

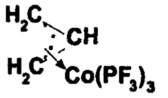


(7)

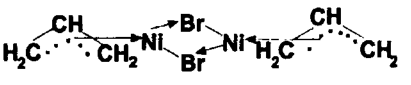
(8)

The same reactants in the presence of triethylphosphine (8) form σ-complex **XII**.[13,16] However, the structures of complexes **XI** and **XII** cannot be confirmed on the basis of available data.

Gas-phase reactions of alkenes and their halogen-substituted derivatives with atomic metals π-allyl complexes. In particular,[7,22] π-allyl complex **XIII** is formed by interaction at 77 K of propene with atomic cobalt in the presence of phosphorus trifluoride. The reaction of bromopropene with atomic nickel at 77 and 298 K is accompanied[22] by the formation of *bis*-allyl derivative **XIV**:

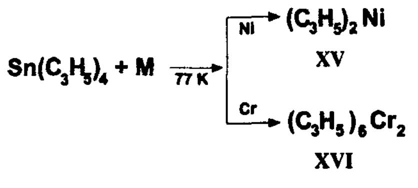


XIII



XIV

Organometallic compounds can serve as a source of allyl ligands, for example in the formation of π-allyl complexes of nickel (9) and chromium (10):[22]



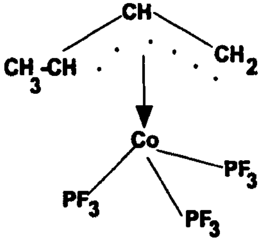
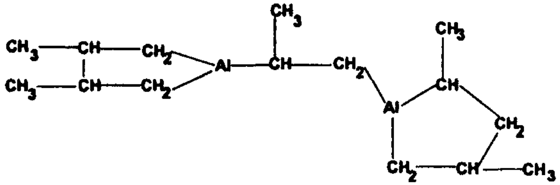
(9)

(10)

However, when choosing olefins as ligands for cryosynthesis, it is necessary to bear in mind that various catalytic transformations of these unsaturated hydrocarbons could take place during co-condensation with metal vapors.

Selected data on metal vapor reactions with alkenes are presented in Table III.

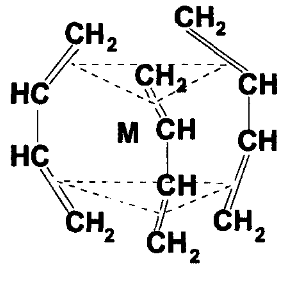
TABLE III Cryosynthesis of metal complexes with olefins

Metal	*Ligand*	*Product*	*T*, K	*Ref.*
Ni, Pd, Au, Li, Co, Cu, *etc.*	C_2H_4	$M_n(C_2H_4)_m$, $n = 1-4$; $m = 1-6$	8–77	22,115,121–126
Ni	$Sn(C_3H_5)_4$	$Ni(C_3H_5)_2$	77	22
Cr	$Sn(C_3H_5)_4$	$Cr_2(C_3H_5)_2$	77	22
Co	$EtCH{=}CH_2 + PF_3$	 + $HCo(PF_3)_4$	77	11,127
Pd	Bicyclo[2.2.1]-heptene (L)	PdL_3	77	128
Li	C_2H_4	$Li(CH_2)_nLi$ $n = 2, 4, 6$	77	125
Cu, Ag	(a) cyclic alkenes (L)	ML	77	129
Cu	$CH_3{-}CH{=}CH_2$		77	11,127

b. Interaction of Metals and Polyenes

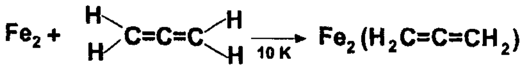
Metal vapor synthesis with non-cyclic diene hydrocarbons form a series of π-complexes, in which unsaturated ligands are η^4-π-donor molecules.[7,11,13,16,22,41,44,45] Most of these π-complexes are derived from 1,3-butadiene, for which five types of coordination compounds having the compositions metal : diene 1 : 1, 1 : 1 : L_n, 1 : 2, 1 : 2 : L_n (L = CO, PF_3, PR_3) and 1 : 3, have been prepared. Complexes of the first type are formed by interaction of 1,3-butadiene with iron at room temperature and 100 Torr,[45] those of the second type by the reactions of diene and trimethoxyphosphine[130] or triphenylphosphine.[117] The formation of the third type of coordination compounds is deemed possible in the cases of cobalt[22] and iron.[107] The fourth (and most common) type of compounds includes iron,[13,41,131] cobalt,[11,13] chromium,[13,132] and ruthenium[44] complexes. In particular, ruthenium forms stable adducts $Ru(\eta^4\text{-}C_4H_6)_2L$, where L = PF_3, CO, Me_3CNS.[44] Complexes of the fifth type, formed by molybdenum and tungsten,[11,127,133] are characterized by X-ray diffraction data, which show equal distances of Mo and W atoms to all carbon atoms of the butadiene ligand and a trigonal prismatic arrangement of the C=C double bonds **XVII**[38] (Figure 2):

The photochemical cryosynthesis (11) of iron complexes with propandiene (allene) in solid argon takes place with high selectivity.[46] Using FTIR-spectroscopy, formation of π-complexes of diatomic iron **XVIII** was observed:



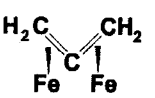
XVII

FIGURE 2 *tris*-(Butadiene)molybdenum (tungsten) structure.

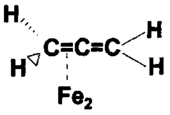


$$Fe_2 + H_2C{=}C{=}CH_2 \xrightarrow[10\,K]{} Fe_2(H_2C{=}C{=}CH_2) \qquad (11)$$

XVIII



XVIIIa

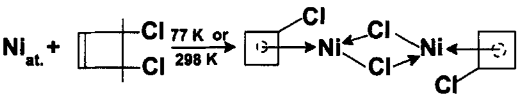


XVIIIb

The structures presented by formula **XVIIIa**, **XVIIIb** were proposed for these π-complexes:

ESR (electronic spin resonance) study of the reaction of ground-state Al atoms with 1,3-butadiene in adamantane at 77 K in a rotating cryostat showed formation of two paramagnetic products: a σ-bonded Al cyclopentene and an Al-substituted allyl.[134] The authors proposed the structure of the first complex with the Al atom below the plane of the butadiene framework at an angle of ~42°, whereas the Al-substituted allyl is possibly a bridged species.

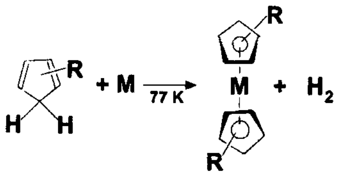
Cyclo-olefin complexes[13,22,47,50] are among the most interesting coordination compounds synthesized through cryosynthesis. Compound **XIX**[22] is an example of a "non-standard" binuclear π-complex, obtained as a result of the following transformation (12):



XIX

(12)

Most η^5-π-coordinated complexes having the general formula **XX** have been obtained from cyclopentadiene and its substituted derivatives,[9,13,16,22,47,49,135,136] which have a very important role in metal vapor chemistry. In this case, the hydrogen atom is lost with a simultaneous aromatization of the ligand (Scheme (13)):



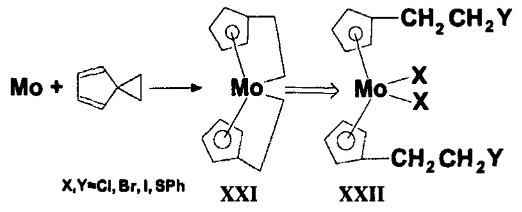
XX

M = Co, Fe, Cr, Mo, W

(13)

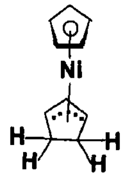
Synthetic conditions were developed for symmetrically substituted heteroannular alkylferrocenes starting from alkylcyclopentadienes (molar ratio ligand : metal is 20–40), which were co-condensed on the surface of the reactor at 77 K with iron vapor. The reactions take place according to Scheme (13), where R = Alkn, M = Fe. The yields of alkylferrocenes are 28% (R = dimethyl), 29% (R = octamethyl), and 72% (R = diethyl).[136]

An interesting series of transformations (14) with spiroderivatives of cyclopentadiene was described.[137] As a result of the interaction of atomic molybdenum with spiro-[2,4]-hepta-4,6-diene **XV** at 77 K, the cyclopentadienyl derivative **XXI** was obtained, from which a series of sandwich molybdenum complexes having general formula **XXII** could be prepared:

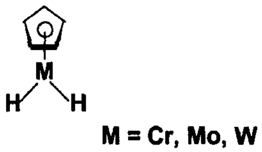


(14)

An intermolecular dehydrogenation–hydrogenation of the cyclopentadienyl ligand takes place in reaction (13) (M = Ni, R = H), forming **XXIII**:



XXIII

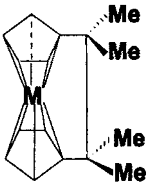


XXIV

In addition to the typical sandwich complexes, the monocyclopentadienyl–hydride complexes **XXIV** have also been isolated by interaction of cyclopentadiene with atomic chromium, molybdenum and tungsten.[13]

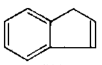
The derivatives of cyclopentadiene with various substituents (L = 1,3-t-Bu_2CpH, 1,2,4-t-Bu_3CpH, $EtMe_4CpH$, M = Co;[138] L = 1,3-t-Bu_2CpH, 1,2,4-t-Bu_3CpH, M = Ni[139]) were obtained by the metal vapor route. The structures of the products were determined by single-crystal X-ray diffraction. Co-condensation of metals with 6,6-dimethylfulvene and spectroscopic study of formed complexes has been carried out.[140,141] Ga, Tl, Cu and Mn form $Cp_iM(I)$ derivatives ($Cp_i = C_5H_4CHMe_2$), however, for Cu and Mn, trimethylphosphite was necessary as a co-ligand to fill the coordination sphere. Cobalt, 6,6-dimethylfulvene and trimethylphosphite led to formation of $CoH[P(OMe)_3]_4$ instead of a half-sandwich complex.[140] Sn and Pb form *anse*-metallocenes **XXV**:[141]

This is one of the very few examples of Pb undergoing direct synthesis to an organometallic complex.[141]

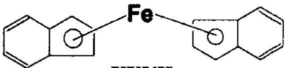


XXV

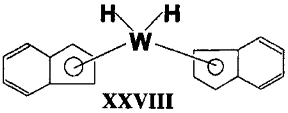
Reaction of a structural analogue of cyclopentadiene – indene **XXVI** – with atomic iron and tungsten leads to compounds **XXVII–XXX**, for which a peculiar bonding isomer is typical. Participation of either cyclopentadienyl or benzene rings in coordination with a metal atom is observed.[22] This interesting phenomenon has been examined in a limited series; the reasons provoking it are still not clear.



XXVI

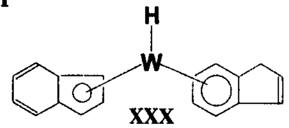


XXVII



XXVIII

XXIX



XXX

Among the mixed-ligand compounds, cyclopentadienylcarbonyl $C_5H_5M(CO)_2$, cyclopentadienylpentamethylcyclopentadienyl $C_5H_5MC_5(CMe_5)_5$, and cyclopentadienylacetylene $C_5H_5M(C_2H_2)_2$ complexes, where M = Rh and Ir, have been cryosynthesized and characterized.[48] The application of the metal-atom technique to the synthesis of Cp-metallaboron clusters was investigated.[142] A series of the products including 1,2,3-$(CpCo)_3B_5H_5$ ($Cp=\eta^5$-cyclopentadienyl), 8-σ-(C_5H_9)-1,2,3-$(CpCo)_3B_5H_4$ and (μ_3-CO)-1,2,3-$(CpCo)_3B_3H_3$ was obtained by reaction of Co vapor and cyclopentadiene with B_5H_9.

Cryosynthesis with metals allows one to produce the π-complexes of cyclohexa-1,3-diene (CHD-C_6H_8), as well as cycloocta-1,3- and 1,5-dienes (CHD-C_8H_{12}).[16,22,50] The compounds formed have compositions MLL'_n, ML_2, ML_2L', where $L=$ diene, $L'=H, CO, PF_3, C_4H_9NC, Ph_2PCH_2CH_2PPh_2$, $M=Fe, Cr, Mn$. The complex Mn(η^4-1,3-CHD)$_2$CO[50] has been obtained by co-condensation of atomic manganese with cyclohexa-1,3-diene and CO at 77 K with further heating of the condensed phase to 93 K. Its structure has been proved by X-ray diffraction.[50] Two compounds from manganese and cycloocta-1,3-diene, having compositions Mn(η^5-C_8H_{11})(CO)$_3$ and Mn(η^3-C_8H_{13})(CO)$_4$, were isolated under the same conditions,[50] through dehydrogenation–hydrogenation of the ligand system.

The details of co-condensation of 1,3- and 1,5-cyclooctadienes with metals are examined in a review[16] and monograph.[22] Among the results presented in a review[16] two must be highlighted: the isomerization of 1,3-CHD to the 1,5-diene ligand system with chromium and the X-ray diffraction proof of the structure of the complex $C_8H_{11}Cr(PF_3)_3H$ as (η^4-cyclooctadienyl)hydrido*tris*(trifluorophosphine)chromium. Additionally, the complex (COD)$_2$Fe, prepared by the metal vapor route, was used for ligand exchange of one COD ligand. The aim was to prepare (COD)(phosphinine)Fe(0) complexes which could be used as novel room-temperature catalysts for pyridine formation.[143]

Synthesis of a series of π-complexes of cyclotrienes[49,144] has been carried out. Thus, interaction of vapors of titanium, vanadium, chromium, and cobalt with cycloheptatriene (C_7H_8) at 77 K leads to the mixed-ligand compounds Ti(η-C_7H_7)(η^5-C_7H_9), V($C_{14}H_{16}$), Cr(η-C_7H_7)(η^4-C_7H_{10}), as well as the *bis*-heptatriene chromium complex.[49] However, it was impossible to isolate complexes of manganese, nickel and palladium with these ligands.

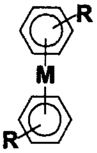
Co-condensation of chromium vapors with cycloheptatriene and trifluorophosphine gave (1-6-η-cyclohepta-1,3,5)-tri-(trifluorophosphine)chromium(0) [$Cr(C_7H_8)(PF_3)_3$]. Its structure was established by IR-spectroscopy and heteronuclear ^1H, ^{13}C, and ^{31}P NMR data.[144] The η^5-cycloheptatrienyl-η^5-cyclopentadienyl iron complex Fe(η^5-C_7H_7) (η^5-C_7H_9), obtained by co-condensation of iron vapors and liquid cycloheptatriene in methylcyclohexane at 143 K, was also characterized.[144] Starting from cycloheptatriene in the conditions of cryosynthesis (77 K), manganese complexes Mn(η^4-C_7H_8)$_2$(CO) and Mn(η^5-C_7H_9)(CO)$_3$ were synthesized,[50] although with low yields. Other complexes prepared from cycloheptatrienes are discussed in reviews.[7,16]

Only a few cyclo-octatetraene (COT) complexes have been obtained by cryosynthesis.[144–146] Information on the syntheses of *bis*(cyclo-octatetraene)uranium $U(COT)_2$, analogous thorium and plutonium complexes, and (COT)-*tris*-(trifluorophosphine)iron $(COT)Fe(PF_3)_3$ is presented in a review.[21] Although the binuclear COT complex $Cr_2(C_8H_8)_3$ was mentioned,[144] its synthesis was not carried out. Additionally, a paramagnetic sandwich complex of *tris*(cyclo-octatetraene)dititanium was described.[146]

Summarized data on the vapor synthesis of metal complexes with dienes, trienes and tetraenes are presented in Table IV.

c. Interaction of Metals and (Het)arenes

Cryosynthesis is especially effective in the preparation of η^6-arene complexes. At the present time, arene π-complexes, **XXXI**, have been obtained from almost all transition metals and various η^6-aromatic ligand systems, which can donate six π electrons to a bound metal:

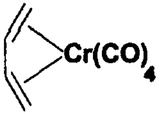
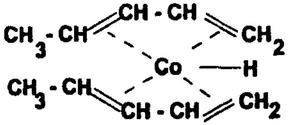
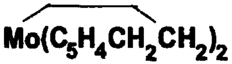
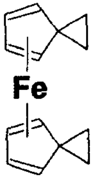


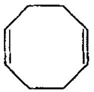
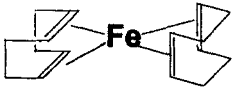
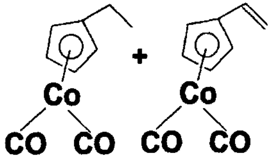
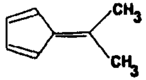
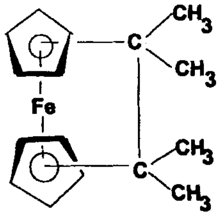
XXXI

The early publications on gas-phase synthesis, properties and structures of complexes of type **XXXI** have been reviewed[5,7,12,16] and constitute the subject matter of a monograph.[22] Among early papers, it is necessary to single out the work of *Graves and Lagowski*,[42] in which thirty-eight *bis*-arene sandwich complexes of type **XXXI** (R = F, Cl, CF_3, Alk, OAlk, $NAlk_2$,COOAlk), obtained by co-condensation of metals and ligands at 77 K and 5×10^{-4} Torr, are described. The complexes were characterized by ^{13}C NMR-spectra and their relative thermal stability was determined.

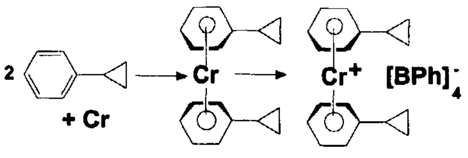
^1H NMR spectroscopy and mass-spectral studies have been used to characterize chromium complexes containing electronegative substituents in the benzene rings **XXXI** (R = F, Cl).[49] These compounds were prepared at 77 K and 10^{-4} Torr. The syntheses of *bis*(benzene)ruthenium,[154] (dicyclopropylbenzene)chromium **XXXII** and its tetraphenylborate derivative **XXXIII**[150]

TABLE IV Cryosynthesis of metal complexes with acyclic and cyclic dienes, trienes and tetraenes

Metal	*Ligand*	*Product*	*T*, K	*Yield*, %	*Ref.*
(a) Acyclic dienes and trienes					
Fe	$CH_2{=}C{=}CH_2$	$Fe_2(CH_2{=}C{=}CH_2)$	10		46
Fe_2	$CH_2{=}C{=}CH_2$, hν	$Fe(HC{\equiv}C{-}CH_3)$	10		
Mo, W	$CH_2{=}CHCH{=}CH_2$ (L)	ML	77		11,127,133
Ni, Fe	Buta-1,3-diene	$M(C_4H_6)$	77,298 (100 Torr)		45,49
Cr, Ru	Buta-1,3-diene + L (PF_3, CO, Me_3CNS)	$M(C_4H_6)_2L$	77		44,147
Cr	$CH_2{=}CHCH{=}CH_2 + CO$		77		11,127
Co	$CH_2{=}CHCH_2CH{=}CH_2$		77		11,16,127
Ni	Cycloocta-1,5-diene	*Bis*(cycloocta-1,5-diene)nickel	77		148
Cu, Ag, Au	Unconjugated dienes (L)	ML	77		129
Mo	Spiro[2,4]-hepta 4,6-diene	 $Mo(C_5H_4CH_2CH_2)_2$	77	50–60	149
(b) Cyclodienes					
Fe, Cr, Mo, W	CpH	$M(Cp)_2$	77	20–100	16,147,150
Fe			77		151

Fe	RC_5H_5, R = Me,Et	$Fe(RC_5H_4)_2$	77	28–72	16
Mn	CpH + CO	$\{Mn(C_5H_5)(CO)_3\}$ + $\{Mn(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_{10}H_{12})(CO)_2\}$	77	6–10	152
Fe			77		74,153
Co	 + CO		77	1	150
Fe	Dimethylfulvene 	 $+[C_5H_4\text{-}C(CH_3)_2H]_2Fe$	77		16
Mn	Cyclohexa-1,3-diene + CO	$\{Mn(C_6H_8)_2(CO)\}$	77	6–10	50
	Cycloocta-1,3-diene + CO	$\{Mn_2(CO)_{10}\}$ + $\{Mn(\eta^3\text{-}C_8H_{13})(CO)_4\}$ + $\{Mn(1\text{-}5\text{-}\eta\text{-}C_8H_{11})(CO)_3\}$			
	Cyclohepta-triene + CO	$\{Mn(\eta^4\text{-}C_7H_8)_2(CO)\}$			
Ti, V, Cr, Fe	Cyclohepta-triene	ML_2	77	15–46	144
Cr, Co Cr, Fe	Cyclohepta-triene + PF_3	$ML(PF_3)_n$			
Ti, Fe, Co, U, Th, Pu	COT	$M(COT)_n$			

were also carried out. The reactions take place according to Scheme (15):

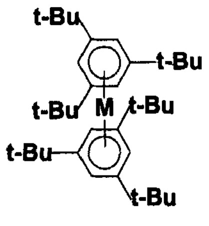


XXXII XXXIII

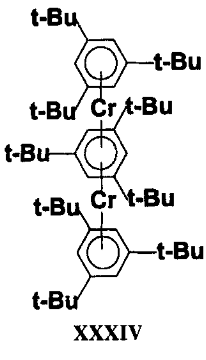
(15)

Under similar conditions, a series of compounds, containing various substituents in the aromatic nuclei (ferrocenyl, yield 1%;[155] CH_2Ph 48%, CH_2CH_2OH, 5% and C_3H_7CO, 4%[156]), have been obtained and characterized.

bis-Arene complexes **XXXIII** having general formula $M(\eta^6\text{-}t\text{-}Bu_3C_6H_3)_2$[52–54] could be prepared by reactions of atomic yttrium, titanium, hafnium, niobium, chromium, molybdenum, and tungsten with 1,3,5-tri-*tert*-butylbenzene, in spite of possible steric problems. Reactions take place at 77 K and allow preparation of products with yields of 20% (M = W), 30–50% (M = Cr, Mo),[54] and 40% (M = Ti, Zr, Hf).[52] In the case of chromium, together with *bis*-arene compound **XXXIII** (M = Cr), a triple decker complex $[Cr_2(\eta^6\text{-}t\text{-}Bu_3C_6H_3)_2(\mu\text{-}\eta^6\text{:}\ \eta^6\text{-}t\text{-}BuC_6H_3)]$ **XXXIV**[54] is formed (yield 2%).

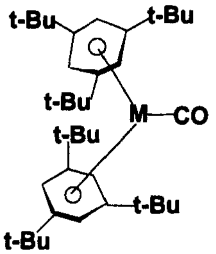


XXXIII

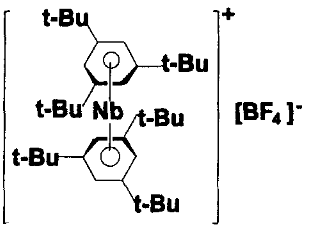


XXXIV

Reactions of zirconium and hafnium with the same ligand in the presence of carbon monoxide lead to formation of a stable 18-electron adduct **XXXV** of zirconium and an analogous hafnium complex of low stability. The interaction of the complex **XXXIII** (M = Nb) with $AgBF_4$ in toluene is accompanied by formation of a tetrafluoroborate complex containing the stable 16-electron cation **XXXVI**.[54]



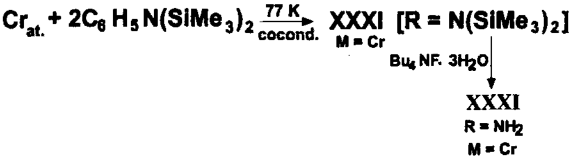
XXXV



XXXVI

Structures of complexes **XXXIII** and **XXXVI** were proven[54] by mass- and ^{1}H NMR-spectroscopy. The yttrium complex **XXXI** (M = Y) is unusual, because it is paramagnetic ($\mu_{eff} = 1.74$ BM at room temperature) and its EPR spectrum in methylcyclohexane shows a well-defined doublet at 77 K. Y: $g_{\parallel} = 2.085$ (doublet), $A = 3.0$ mT, $g_{\perp} = 2.005$. A preliminary X-ray diffraction study[53] showed that yttrium and gadolinium complexes contain parallel benzene rings and constitute the first examples of η^6-coordination of these metals.

In spite of the fact that the chromium complex **XXXI** with a dialkylamino substituent (M = Cr, R = NMe$_2$) has been known for more than twenty years[42] and its structure was proven by X-ray diffraction,[157] it has been impossible to prepare an analogous complex with aniline. Some years ago,[43] the complex **XXXI** {M = Cr, R = N(SiMe$_3$)$_2$} was obtained by co-condensation of chromium atoms with *bis*(trimethylsilyl)aminobenzene at 77 K. The synthesized compound, after treatment with tetrabutylammonium fluoride hydrate in THF at 298 K, produced *bis*(aniline)chromium **XXXI** (M = Cr, R = NH$_2$). The described transformation takes place according to Scheme (16):



$$Cr_{at.} + 2C_6H_5N(SiMe_3)_2 \xrightarrow[\text{cocond.}]{77\,K} \underset{M\,=\,Cr}{XXXI}\ [R = N(SiMe_3)_2] \xrightarrow{Bu_4NF.\,3H_2O} \underset{M\,=\,Cr}{\underset{R\,=\,NH_2}{XXXI}} \qquad (16)$$

The complex **XXXI** (M = Cr, R = NH$_2$, m.p. 501 K) was characterized by elemental analysis, ^{1}H and ^{13}C NMR and mass-spectroscopy; its reduction potential and Bronsted basicity were studied. Upon interaction between *bis*(π-aniline)chromium and its π-N,N-dimethylaniline analogue with HBF$_4$ in diethyl ether, protonation takes place on the nitrogen.

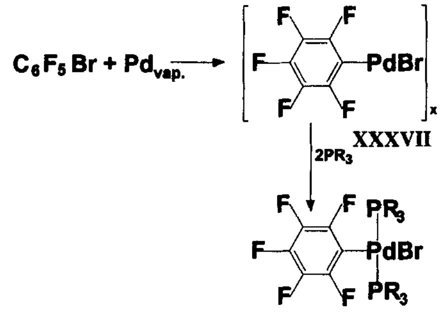
bis-π-arene complexes of such metals as titanium have been described.[43,158] Thus, the complex **XXXI** ($M = Ti$, $R = Et$) was prepared by interaction of ethylbenzene with titanium at 77 K in vacuum with ~100% yield.[158] Among the sandwich complexes of polynuclear arenes, the synthesis and characterization of *bis*-η^6-naphthalene chromium were reported.[159] In this work a series of coordination compounds having the general formula $(\eta^6\text{-Ar})CrL_3$, where $ArH = C_{10}H_8, C_{10}H_7Me, C_{10}H_6Me_2$; $L = CO, PMe_3, P(OMe)_3, PF_3$ (co-ligands), was synthesized by co-condensation at 193 K of atomic chromium and naphthalene or its methyl-substituted derivatives. The obtained compounds were characterized by ^{1}H NMR spectroscopy. It was emphasized that atomic chromium interacts with 1,4-dimethylnaphthalene regiospecifically, forming mainly (*ca.* 95%) the isomer in which the metal atom is bound to the unsubstituted aromatic nucleus.

Various metal-arene and hetarene complexes have been isolated $[(i\text{-PrO})_2B\text{-}\eta^6\text{-}C_6H_5]_2M$ ($M = Cr, V$) bearing boryl substituents;[160]*hexakis*-(η^1-phosphabenzene)chromium(0) which could be also prepared by ligand substitution at *bis*-(2,4-dimethyl-η^5-pentadienyl)chromium;[161a] $[C_5(CMe_3)_3H_2P]_2M$ ($M = Ho$;[161b] $M = V, Cr$[162]), *bis*-(η^6-bimesityl)-chromium,[162] numerous π-arene complexes of chromium and other transition metals,[163–168] including mononuclear *tris*(arene)-metal complexes described in a review.[169]

Yurieva et al. published a review[56](see Table V), is devoted to (*bis*-arene)chromium complexes of aromatic compounds, containing other groups, which are active toward metal atoms (the phosphorus atom in a triphenylphosphine substituent, C≡C- and C≡N-bonds), as well as polynuclear fragments (α,ω-diphenylalkanes, diphenylacetylene). Thus η^6- and η^{12}-coordinated mono- and binuclear chromium complexes are formed as a result of the interaction between atomic chromium and 1,4-diphenylbutane and 1,5-diphenylpentane. This is the first example of a one-step synthesis of bridging compounds of the dibenzenechromium series.

Using a mixture of benzonitrile with other monosubstituted derivatives of benzene (ArR, $R = H, OMe, COMe, CF_3, F, Cl$) in the reactions with atomic chromium, a series of complexes $(PhCN)_2Cr$, $(PhCN)Cr \cdot (PhR)$ and $(PhR)_2Cr$ was synthesized in low yield (from 0.6% to 10%). The corresponding tetra-substituted chromium η^6-complexes were prepared by co-condensation of Cr vapors with di-substituted derivatives of benzene, containing, together with the F-, Me-, MeO- and Cl-substituents. According to ^{19}F NMR data, two diastereomers form as a result of such transformations: the first is a racemic mixture of two enantiomers, the second is a *meso*-form.[56]

Organometallic compounds of arenes containing σ metal–carbon bonds are also prepared by the technique above. Thus, the complexes [RuH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] and [OsH(η-C_6H_6)(PMe_3)(σ-C_6H_5)] were synthesized by co-condensation of the corresponding metal atoms with C_6H_6 and PMe_3.[170] Using C_6F_5Br in co-condensation with palladium atoms, an orange-brown powder of $(C_6F_5PdBr)_x$ **XXXVII** is formed, instead of the expected η^6-complex with participation of benzene rings (17):



(17)

The product is stable to air and moisture, soluble in organic solvents (where it is found to be dimeric and trimeric), and very reactive with *Lewis* bases.[38]

The stability, physico-chemical properties and electronic structure of *bis*-arene complexes, as well as their syntheses and decomposition, have been studied systematically.[5,7,12,16,43,157,171–175] In particular, the feasibility of using additive methods to calculate ΔH_f of vaporous metal *bis*-arene complexes was examined.[175] The electronic[176,177] and fluorescent[178] spectra of molybdenum complexes were interpreted, and oxidation–reduction properties of *bis*-arene derivatives of transition metals[179] were discussed. Activation mechanisms of benzene derivatives by lithium atoms are described.[180,181] The model reaction is developed using the spectroscopic results and *ab initio* calculations.

For *bis*-arene metal complexes, it is possible to present and discuss the mechanism of direct cryosynthesis. It is known[16] that, for decomposition of dibenzenechromium

$$(C_6H_6)Cr(g) \Leftrightarrow Cr(s) + 2C_6H_6(g) \qquad (18)$$

the equilibrium constant is increased with temperature from 298 to 1000 K. The magnitude of ΔG between 298 and 800 K and pressures of 10^{-5}–10^{-7} atm was also studied at 10^7 atm ΔG changes its sign, *i.e.* equilibrium is moved to dibenzene chromium formation. In order to establish a reaction mechanism (the direct reaction could be gas-phase or "gas–solid"), it is possible to calculate the change of ΔG (kcal/mol) for the following processes which occur in these conditions (chromium atoms were considered as ideal gas):

$$\mathrm{Cr(s)} + 2\mathrm{C_6H_6(g)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(g)} \quad \Delta G = 27.2 \tag{19}$$

$$\mathrm{Cr(s)} + 2\mathrm{C_6H_6(g)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(s)} \quad \Delta G = 18.9 \tag{20}$$

$$\mathrm{Cr(g)} + 2\mathrm{C_6H_6(g)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(g)} \quad \Delta G = -57.4 \tag{21}$$

$$\mathrm{Cr(g)} + 2\mathrm{C_6H_6(g)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(s)} \quad \Delta G = -65.5 \tag{22}$$

$$\mathrm{Cr(g)} + 2\mathrm{C_6H_6(liq)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(s)} \quad \Delta G = -62 \tag{23}$$

$$\mathrm{Cr(s)} + 2\mathrm{C_6H_6(s)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(s)} \quad \Delta G = 16.4 \tag{24}$$

$$\mathrm{Cr(g)} + 2\mathrm{C_6H_6(g)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(s)} \quad \Delta G = -70 \tag{25}$$

$$\mathrm{Cr(g)} + 2\mathrm{C_6H_6(g)} \Leftrightarrow \mathrm{(C_6H_6)_2Cr(g)} \quad \Delta G = -30.3 \tag{26}$$

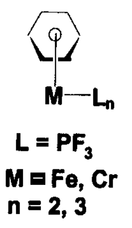
It is clear that reactions (21–23, 25, 26) are thermodynamically possible. On the basis of experimental results, it was concluded that an equilibrium of the reactions (19, 20, 24) was moved to reactants, since chromium powder, which is formed as a result of aggregation of atomic metal in the absence of reaction with benzene remains in the reaction chamber.

Moreover, the thermodynamically permitted reactions (21, 22, 26) require trimolecular collisions, the probability of which is almost zero. For gas-phase reactions, the possibilities (z_3) of trimolecular and bimolecular (z_2) collisions are $z_3/z_2 = 10^{-2}P$, where P is the pressure in atm and $T = 300\,\mathrm{K}$. In the conditions of cryosynthesis, the magnitude P is 10^{-6}–10^{-8} atm, so $z_3 = (10^{-8}-10^{-10})z_2$ is extremely low. At this pressure the distance required for a metal atom is much more than the dimensions of any type reaction chamber used, it is evident that cryosynthesis is a "gas–solid phase". In this case, the gas is the metal and the solid is benzene. On this basis, a mechanism of cryosynthesis was proposed.[16]

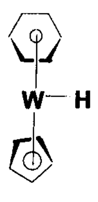
A metal atom, arriving to the surface of the condensed (in)organic substance loses its energy in the first collision with condensed phase molecules (it could be concluded from an evaluation of the kinetic energy of a flying atom). A local over-heating of the condensed phase contributes to diffusion of metal atoms and molecules of the organic phase; as a result, a favorable orientation of the reaction's participants in the matrix (for the subsequent interaction) is reached.

When a metal is evaporated intensively, the possibility of aggregation of its atoms increases. Moreover, an insufficient heat exchange and thick layer of (in)organic phase on the chamber walls could provoke a melting of this phase (reaction (23)). The "gas–liquid" reaction is thermodynamically favorable; however, in these conditions aggregation of metal atoms is specially high. Metal in the condensed form does not react. The reduction of yield of dibenzenechromium and formation of metal powder as a result of this reaction could be explained by this, although the yield is also determined by decomposition of the product.

In addition to the *bis*-arene compounds of types **XXXI–XXXIII**, the monoarene, for example **XXXVIII**, and "mixed-ligand" cyclopentadienyl-arene **XXXIX** complexes were obtained by co-condensation of atomic metals and mixtures of corresponding ligands.[5,16,97]

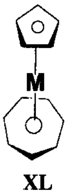


XXXVIII

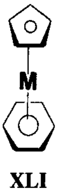


XXXIX

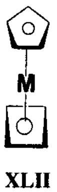
Other "mixed-ligand" compounds of the types **XL–XLIII**



XL



XLI

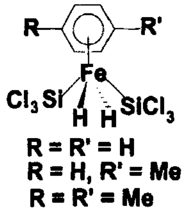


XLII

XLIII

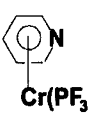
which have been synthesized by conventional chemical methods,[38] could also be obtained by interaction of metal atoms with a mixture of the corresponding ligands (see 56 and Table V).

Unusual iron(IV) complexes of composition (η^6-benzene)$Fe(H)_2(SiCl_3)_2$, (η^6-toluene)$Fe(H)_2(SiCl_3)_2$, (η^6-*p*-xylene)$Fe(H)_2(SiCl_3)_2$ **XLIV** were obtained from "solvated iron atoms" in the corresponding solvent (benzene, toluene or *p*-xylene), prepared by co-deposition of solvent with iron vapor, and $HSiCl_3$.[182] The novel π-arene products were characterized by X-ray diffraction data and ^1H NMR spectroscopy. These results show that there is no chemical interaction between Si and H or between H and H atoms in these compounds.[182]

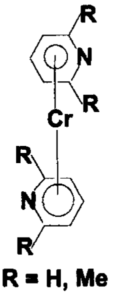


XLIV

In addition to the noted *hexakis*(η^1-phosphabenzene)chromium(0) and *bis*(2,4,6-tri-*tert*-butyl-phosphorin)holmium(0),[161] complex compounds of heteroaromatic systems, obtained under cryosynthesis conditions, are represented by π-complexes of pyridine and its C-methyl-substituted derivatives. In fact, the possibility of participation of the pyridine π-system as a ligand was first shown when the π-complex **XLV** was prepared by co-condensation of atomic chromium with pyridine in the presence of PF_3 as a co-ligand.[7] The low-temperature reaction between atomic Cr and 2,6-dimethylpyridine led to the first sandwich π-complex of an azine (although with a low yield – 2%): *bis*(2,6-dimethylpyridine)chromium **XLVI** (R = Me).[57] Its structure was proved by X-ray diffraction.[57,183] Similar compounds were isolated using Ti, Mo and V vapors.[184] The authors of 184 noted that other syntheses of *bis*(η^6-2,6-dimethylpyridine)metal complexes were unsuccessful, probably as a result of nitrogen lone pair-metal σ or C–H-metal reaction pathways. Using trimethylsilyl derivatives of pyridine in the same synthesis, it is possible to also prepare a parent of *bis*(η^6-azine) metal complexes: *bis*(η^6-pyridine) **XLVI** (R = H).[185] We emphasize that it was impossible to obtain any of the *bis*(η^6-pyridine)metal complexes by conventional synthetic procedures.[186,187]

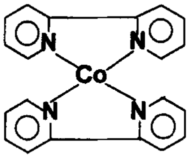


XLV



XLVI

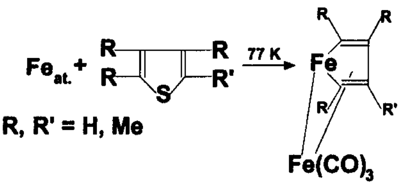
Azines could interact with atomic metals cryosynthetically to give N-σ-complexes. This type coordination compound was obtained by co-condensation at 77 K of chromium vapors with α,α'-bipy **XLVII**.[58]



XLVII

This compound was studied by IR, UV, and EPR spectroscopy and by determination of its magnetic properties.[58] Its μ_{eff}, determined by *Faraday*'s method, of 2.02 BM, indicated one unpaired electron for the electronic configuration of **XLVII**. This complex undergoes chemical (Br_2, tetracyanoethylene and tetracyanoquinodimethane) and electrochemical oxidation.[58]

Although a review[188] indicates that thiophene does not react with metals, the transformation (27) is known[22]



XLVIII XLIX (27)

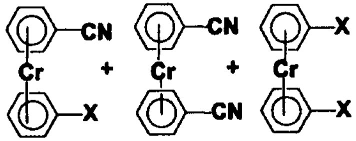
with desulfuration of the heterocycle **XLVIII** and formation of bimetallic complex **XLIX**. Heteroaromatic systems have a real π-donor activity.[188-190]

Summarized data on vapor synthesis of metal arene and hetarene complexes are presented in Table V.

d. Interaction of Metals and Alkynes

Interaction of metal atoms with acetylene and substituted derivatives under cryosynthesis conditions leads mainly to formation of complexes ML_n, where L is C≡CR, and products of tri-, tetra- and poly-alkynes.[6,14,16,22,33,45,46,152,200] In the early work it was considered[22] that, benzene and its substituted derivatives were the main products, and that only

TABLE V Cryosynthesis of metal complexes with arenes and hetarenes

Metal	*Ligand*	*Product*	*T*, K	*Yield*, %	*Ref.*
Cr, Nb, V, Cr, W, Ti, *etc.*	PhR; R = Alk, CF_3, OR, Hal, NR_2, COOR,H	$M(PhR)_2$	77	2–60	11,16,56,106,147, 151,191–194
Fe,Cr	C_6H_6, PF_3	$Fe(C_6H_6)(PF_3)_2$	77		188
Ni	C_6F_6	$Ni(C_6F_6)$	77		191,195
Cr	$PhCH_3$	$Cr(PhCH_3)_2$	77	60	147
	PhC_2H_5	$Cr(PhC_2H_5)_2$	77	52	
K	Arene, THF,MX_n (M = Ti, V, Cr, Mo, X = Hal)	$M(arene)_2$	173		6
K	$MoCl_5$+$PhCH_3$	$Mo(PhCH_3)_2$	173	40	192,196
	$VCl_3 \cdot 3THF$+toluene	$V(PhCH_3)_2$		30	
	$TiCl_3 \cdot 3THF$+toluene	$Ti(PhCH_3)_2$		20	
	$TiCl_3 \cdot 3THF$+mesytilene	$Ti(C_6H_3Me_3)_2$		15	
Cr	Cumene	$Cu(cumene)_2$	77	19	188
Cr	C_6H_6, C_6F_6	$Cr(C_6H_6)(C_6F_6)$	77		106
Cr	o-$ClC_6H_4CF_3$	Cr(o-$ClC_6H_4CF_3)_2$	77	33	191,192
Cr	PhCN	$Cr(PhCN)_2$	77		56
Cr	PhCN+PhX (X = H,CH_3,OCH_3, Cl, F, CF_3, CN)		77		56
Cr	p-XC_6H_4F (L) X = CH_3, CO_2CH_3,Cl	CrL_2	77		56
Pt, Pd	C_6F_5X, PEt_3 X = Cl,Br	$(PEt_3)_2MX_2$+$(C_6F_5)_2$ $(PEt_3)_2M$ $(PEt_3)_2M(C_6F_5)X$	77	3–66	197,198

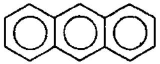
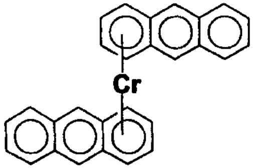
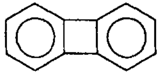
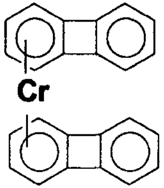
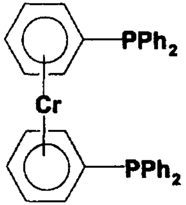
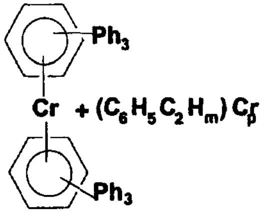
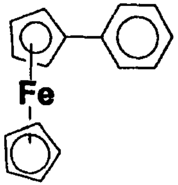
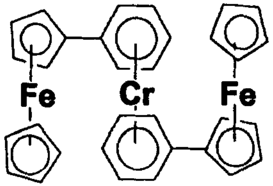
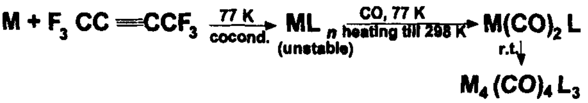
Pt	C_6H_5Br, PEt_3	$(C_6H_5)_2(PEt_3)_2Pt$	77	3	198
Ni, Co	C_6F_5Br, C_6H_6	$M(C_6H_6)(C_6F_5)_2$	77		106
Cr	$PhCH_2OCH_2Ph$	$Cr(PhCH_2OCH_2Ph)$	77		56,74
Cr			77		74
Cr			77		74
Cr		*Bis*(η^6-naphthalene)-chromium(0)	193	43	159,199
K	$CrCl_3(THF)_3$ + naphthalene	$Cr(C_{10}H_8)_2$	163	36	196
	$VCl_3(THF)_2$ + 1-methyl-naphthalene	$V(C_{10}H_7Me)_2$			25
	$CrCl_3(THF)_2$ + 1-methyl-naphthalene	$Cr(C_{10}H_7Me)_2$			40
	$MoCl_5$ + 1-methyl-naphthalene	$Mo(C_{10}H_7Me)_2$			42

TABLE V (*Continued*)

Metal	*Ligand*	*Product*	*T*, K	*Yield*, %	*Ref.*
Cr	PPh_3		77		56
Cr	PhC≡CH		77		56
Cr			77		56

some reactions, for example (28, 29), lead to adducts with metals.[6,22]



$$\mathrm{M + F_3CC{\equiv}CCF_3 \xrightarrow[\text{cocond.}]{77\,K} \underset{(\text{unstable})}{ML_n} \xrightarrow[\text{heating till 298 K}]{CO,\,77\,K} M(CO)_2L \xrightarrow{r.t.} M_4(CO)_4L_3} \tag{28}$$

$$\mathrm{Fe + Me_3SiC{\equiv}CSiMe_3 \xrightarrow[\text{cocond.}]{77\,K} Fe(Me_3SiC{\equiv}CSiMe_3)} \tag{29}$$

A large variety of complexes of alkynes ML_n formed from almost all metals of the Periodic Table is presented in a review.[14] Thus, alkali metals form complexes with acetylene in argon matrices;[201] adducts of aluminum, gallium, copper, and nickel[200] were also described. An ESR spectroscopic study of the reaction of ground-state Al atoms with acetylene in cyclohexane and adamantane at 77 K demonstrated that *trans*-η^1-aluminovinyl, AlCHCH is the initial paramagnetic product which disappears on warming to 100 K. A second aluminum species is formed in adamantane with magnetic parameters which indicate that it is not the π-complex η^2-Al(CHCH) or aluminovinylidene, $AlCHCH_2$, but may be a hydrogen-bridged isomer. Ga atoms give the species, Ga(CHCH), with two magnetically equivalent H and C nuclei that is either a η^2-, π- or σ-complex.[202]

The compounds $M(\pi\text{-}C_2H_2)_n$, where $n = 1, 2$, M = Ni,[200] Fe,[45] and Cu,[33,200] are formed by co-condensation of these transition metals with acetylene at 10 K. It is interesting that the complex of iron with monomethylacetylene L has been also obtained by reaction of allene with iron atoms at 10 K (argon, irradiation by visible light).[46] The reaction takes place according to the following Scheme (30):

(30)

Under UV-irradiation L yields two σ-organometallic complexes: $H{-}Fe{-}C{\equiv}C{-}CH_3$ and $H_3C{-}Fe{-}C{\equiv}C{-}C{-}H$.[46] Formation of σ-complexes under cryosynthetic conditions is also observed for other metals.[14] As shown above (Part 3.b) mixed-ligand complexes, for example $C_5H_5Mn(HC{\equiv}CH)_5$,[48] could be formed by co-condensation of acetylene, cyclopentadiene and metals.

A series of metal–alkyne complexes $L_2M(RC_2R')$, where $L = Ph_3P$, M = Ni, Pd, Pt, $R = R' = CF_3$; $L = Ph_3P$, M = Ni, Pt, $R = R' = Ph$, and $R = Ph$, $R' = Me$; $L = Ph_3P$, M = Pd, Pt, $R = R' = COMe$; and $R = R' = CF_3$,

$M = Pd, Pt$, $L = n\text{-}Bu_3P$, Me_2PhP are described.[203] The IR-spectra indicate strong bonding of the alkyne molecule to the metal.

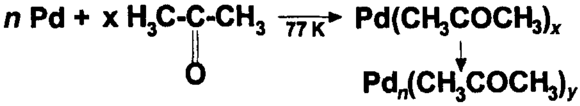
Various types of di-, oligo- and polymerization, take place between atomic metals and alkynes in gas-phase reactions, and are summarized in reviews.[14,16] As an example, atomic nickel reacts with $RC{\equiv}CR'$ ($R,R' = H, Me, Et, Bu, Ph$) to form Ni-alkyne polymers, substituted benzene and COT.[14] A situation close to that described above is observed in the case of co-condensation between ethynes and atomic iron.[14]

The bonding in alkyne complexes of various metals is discussed in detail.[14] The bonding of acetylene to copper atom, dimer, and trimer is discussed.[204] It is shown that the $Cu{-}C_2H_2$ complex has a C_8 structure and a BE of 10 kcal/mol. Three isomers of $Cu_2C_2H_2$ have similar total energies: a C_{2v} end-bonded structure with a BE of 18 kcal/mol, and two-1,2-dicupro ethylene isomers – a *cis* form with a BE of 12 kcal/mol and a *trans* form with a BE of 15 kcal/mol. Two stable isomers of $Cu_3C_2H_2$ were also found.[204]

Summarized data on vapor synthesis with participation of alkynes are reported in Table VI.

e. Interaction of Metals with Other Ligands

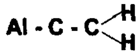
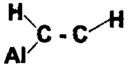
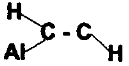
There are few examples of complexes obtained from atomic metals and oxygen-containing ligands. Phenols and aromatic alcohols, ethers, ketones and acids behave as normal η^6-ligands, forming *bis*(η^6-arene) metal-substituted derivatives of type **XXXI** ($R = CH_2CH_2OH$,[156] OAlk,[13,16] COAlk,[156] COOAlk;[16] Alk = Me, Pr). Alcohols form metal alcoholates through cryosyntheses.[16] Stable complexes,[59] forming colloid systems in non-aqueous solutions with particle size ~8 nm, are obtained by interaction between acetone and atomic palladium. It is proposed,[59] that in this case the reaction (31) takes place:



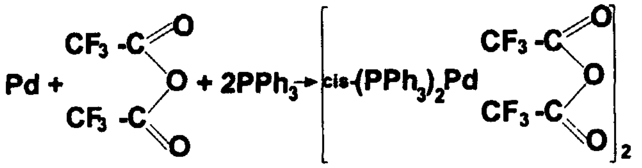
$$\begin{aligned} n\,Pd + x\,H_3C\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_3 \xrightarrow[77\,K]{} \; & Pd(CH_3COCH_3)_x \\ & \downarrow \\ & Pd_n(CH_3COCH_3)_y \end{aligned} \tag{31}$$

However, the structures of the products have not been studied in detail. Oxidative addition (32) takes place under interaction of palladium with

TABLE VI Cryosynthesis of metal complexes with alkynes

Metal	*Ligand*	*Product*	*T*, K	*Yield*, %	*Ref.*
Li, Na, K, Cs	C_2H_2	$M^+\{HC_2H\}^-$	77		14
Al	C_2H_2	3 possible isomers of the adducts Al–C_2H_2 The vinylidene adduct  The *cis*-vinyl adduct  The *trans*-vinyl adduct 	77		14
Ni, Cu	C_2H_2	$M(C_2H_2)_n$, $n = 1, 2$	10–12		200
Au	C_2H_2	$Au(C{=}CH_2)$	77		14
Mn	$C_2H_2 + CpH$	$(Cp)Mn(C_2H_2)_2$	77		48
Er	C_2H_2	$\{ErC_9H_{15}\}_n$, $n = 2, 10$	77		14
Ge	C_2H_2	$(C_2H_{2.7}Ge_{0.72})$ polymer	77	66	205
Sn	C_2H_2	$(C_2H_{2.6}Ge_{0.70})$ polymer		29	
Co	CpH + but-2-yne + penta-borane (9)	(a) $\{2,3\text{-}(CH_3)_2\text{-}1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_4\}$ (b) $\{2,3\text{-}(CH_3)_2\text{-}1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_3\}$ (c) $\{2,3\text{-}(CH_3)_2\text{-}1,7,2,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_5\}$	77		14
Fe	$CH_3C{\equiv}CCH_3$	$Fe(CH_3C{\equiv}CCH_3)_5$	77		14
Fe, Ni	$C_2H_5C{\equiv}CCH_3$	$Fe(C_2H_5C{\equiv}CCH_3)_5$ $Ni/C_2H_5C{\equiv}CCH_3$ pol.			
Ni, Pd	$CF_3C{\equiv}CCF_3 + CO$	$M(CO)_2CF_3C{\equiv}CCF_3$	77		6
Sm, Yb	Hex-3-yne	SmC_6H_{10} YC_6H_{10} probably	77		14
Fe	$PhC{\equiv}CCH_3$	$Fe(PhC{\equiv}CCH_3)_5$	77		14

trifluoroacetic anhydride in the presence of triphenylphosphine:[16]


(32)

LI

It is known[12,13] that the interaction of acyl halides with atomic metals leads to insertion of the metal into the C–Hal bond. An example is the following transformation (33):

$$\mathrm{Pd_{at}} + n\mathrm{RCOCl} \rightarrow n\mathrm{RCOPdCl} \quad (\mathrm{R} = \mathrm{CF_3}, \mathrm{C_3F_7}) \qquad (33)$$

As a result of the co-deposition of Co vapor with C_6F_5Br, the π-complex $Co(C_6F_5)_2$ is formed; workup of which in toluene yields $[\eta^6\text{-}C_6H_5CH_3(C_6F_5)_2Co]$.[193] An X-ray structure of this compound reveals 2 σ-bonded F-phenyl rings with a Co–C bond distance of 1.931 Å; the Co–C(toluene) π-bond distance is 2.141 Å. However, the interaction between Pd atoms and the same ligand, gives the σ-organometallic complex $(C_6F_5PdBr)_x$[38,197] (see Part 3.c).

Metal insertions have also been used in preparation of some RMHal, ArMHal, and RCOMHal complexes with other metals (M = Al, Ni, Pt, Co, Fe, Mn, *etc.*), in particular from highly active metal slurries obtained by metal atom-solvent co-condensations.[74,206] Synthesis, isolation and reactions of coordinatively unsaturated organometallic compounds containing both σ and π bonds are described.[207]

Various perfluoroalkylzinc halides with composition RZnI have been prepared from the zinc atoms at liquid nitrogen temperatures.[74,208] These compounds are unstable and decompose rapidly upon warming (77 K). It is noted that only perfluoroalkyl iodides react with zinc vapor.[74]

Reactions of metal vapors with (in)organic **radicals** leading to metal alkyls and other σ-bonded metal compounds are reported.[209–211] Thus, the radical $\cdot SiF_3$, obtained from a glow discharge of hexafluorodisilane, reacts at low temperature with metal atoms giving $M(SiF_3)_n$ (M = Hg, Te, $n = 2$; M = Bi, $n = 3$) in moderate to high yields.[210] The radicals $\cdot CF_3$ with Pd and Ni vapors give unstable, unsaturated $M(CF_3)_2$ which, when stabilized by trapping with PMe_3 at low temperatures, give *trans*-$(CF_3)_2Pd(PMe_3)_2$ and $(CF_3)_2Ni(PMe_3)_3$.[211]

Vapor syntheses with organohalide derivatives and acyl anhydrides are summarized in Table VII.

TABLE VII Cryosynthesis of metal complexes with organohalide derivatives and acyl anhydrides

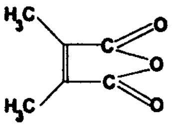
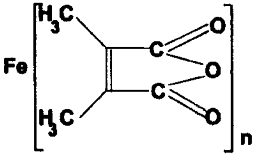
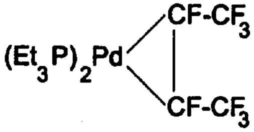
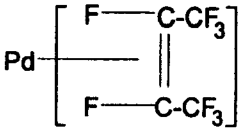
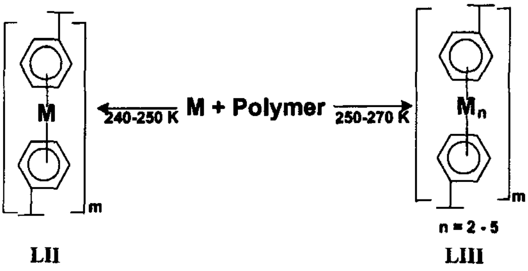
Metal	*Ligand*	*Product*	*T*, K	*Yield*, %	*Ref.*
Pd	$PhCH_2Cl$	$PhCH_2PdCl$	77		13
Pd	n-C_3F_7COCl	$C_3F_7COPdCl$	77		191
	CF_3COCl	$CF_3COPdCl$			
	C_6F_5Br	C_6F_5PdBr			
Ca	C_6F_6	C_6F_5CaF	77		191
Zn	CF_3I	CF_3ZnI			
Fe			77	10–15	16
Fe	PhBr	$(PhPdBr)_n$	77		106
Ag	$(CF_3)_2CFI$,	$(CF_3)_2CFAg$	77		151
Ag	$(CF_3)_2CFI$, c-C_4H_8, CH_3CN	$(CF_3)_2CFAg \cdot CH_3CN$	77	5	212
	CF_3I	CF_3AgI	195	10	
	C_3F_7I	$CF_3CF_2CF_2Ag$	195		
Mg(^{1}S)	C_3H_7Cl	C_3H_7MgCl	77,153	75	11
Mg(^{3}P)	C_3H_7Cl	$CH_3CH{=}CH_2 + C_3H_7 + n$-$C_6H_{14}$	77	35	11
				34	
Pd	CF_3Br	$(CF_3PdBr)_n$	77		194
	C_3F_7COCl, PEt_3	$C_3F_7COPdCl$		15	
	$(CF_3CO)_2O + PEt_3$	*cis*-$(PEt_3)_2Pd(OCOCF_3)_2$		15	

TABLE VII (*Continued*)

Metal	*Ligand*	*Product*	*T*, K	*Yield*, %	*Ref.*
	$CF_3CF{=}CFCF_3 + PEt_3$				
	$CF_3CF{=}CFCF_3$				
Pd	$RCOCl, PEt_3; R = n\text{-}C_3F_7, CF_3, CH_3, n\text{-}C_3H_7$	$(PEt_3)_2Pd(RCO)Cl$	77	4–19	197
Mg, Al, Ga, In	CH_3Br	CH_3MBr	77	213	
Pd	$RX, PEt_3; R = CF_3, C_2F_5, n\text{-}C_3F_7, CCl_3; X = Cl, Br, I$	$(PEt_3)_2PdRX + (PEt_3)_2PdX_2$	77	0–40	197
Pt	$PhCH_2Cl + P(OEt)_3$	$(PhCH_2)\{P(OEt)_3\}_2PtCl$	77	45	198
	CF_3COCl	$(CF_3CO)Pt(CO)Cl$		27	
	CF_3COCl, PEt_3	$(CF_3CO)(PEt_3)_2PtCl$		57	
	CF_3I, PEt_3	$(PEt_3)_2PtI_2 + (PEt_3)_2(CF_3)PtI$		12	
				26	
Ni	Simple alkyl-, fluoro- and chloroolefins	$Ni(olefin)_2, n = 1-3$	10–77		116,214
Ni	$CH_2{=}CHBr$	π-allyl nickel halides	77	75	215
Ni, Pd	$RX\ (X = Cl, Br, I; R = C_6F_5, C_6H_5, CF_3, C_3F_7, C_3H_7)$	RMX	77		16
Pd	$(CF_3CO-)_2O$	$\{(CF_3CO-)_2O \cdot Pd\}$	77		16
	$(CF_3CO-)_2O + PPh_3$	$cis\text{-}\{(CF_3CO-)_2O \cdot Pd(PPh_3)_2\}$			
Mg	$n\text{-}C_3H_7I$	C_3H_7MgI (unsolvated)	77	76	74
	$(CH_3)_2CHBr$	$(CH_3)_2CHMgBr$		55	
	$(CH_3)_3CBr$	$(CH_3)_3CMgBr$		5	
	PhCl	PhMgCl		58	
	$CH_2{=}CHBr$	$CH_2{=}CHMgBr$		78	

f. Interaction of Metals and Polymers

Cryosynthesis for complexes of type **XXXI** is of significance for the preparation of metal-containing polymers.[216–220] Thus, metal-containing polymers of titanium **LII** and **LIII**,[216,218,220] vanadium,[216,218,220] chromium,[216,218–221] molybdenum,[216–218,220] and tungsten[216,218,220] have been synthesized from poly(methylphenylsiloxane). The reactions were carried out by co-condensation of metal vapors and polymers at 240–270 K according to the following general Scheme (34):



(34)

Reaction (34) takes place in steps. The mono-, di-, and trinuclear polymers[216,218] were isolated for chromium; in the case of molybdenum $n = 1-5$.[217] Both homo- and heterometallic polymers have been described; obtained by simultaneous or successive evaporation of different metals. Polystirole could also be used in this type of transformation.[220]

For reaction (34), it is necessary to emphasize the following aspects: (1) this transformation opens the way to synthesize coordination metal polymers;[222–226] (2) it is possible to obtain metal-graphites.[226]

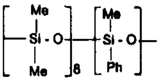
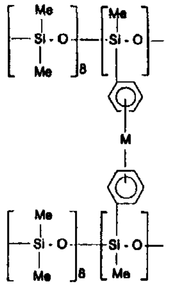
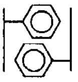
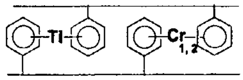
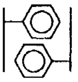
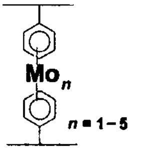
Some reactions of metal atoms with polymers are presented in Table VIII.

4. VAPOR SYNTHESIS OF METAL CHELATES

Practically all metal chelates obtained by cryosynthesis, are β-diketonates of transition and non-transition metals.[7,60,41] This is explained by high stability of β-diketonates and their precursors (β-diketones) in the conditions of gas-phase synthesis at high and low temperatures.

The cryosyntheses of metal acetylacetonates general formula $M(acac)_2$, where M = Mn, Cr, Fe, Ni, Pd, Cu, Zn, Sn, Pb, and $M(acac)_3$, where M = Al,

TABLE VIII Cryosynthesis with use of polymers

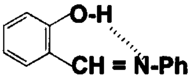
Metal	*Ligand*	*Product*	*T*, K	*Ref.*
Ti, V, Cr Mo, W	Poly(methyl-phenyl sil-oxanes 	*bis*(η^6-arene) complexes (arene = SiO(Ph) groups) 	77, 273	6,227–229
Ti + Cr simultan.			253	216
Mo, Ti, Cr, V			250	217,219,230

Cr, Fe, Dy, Ho, Er, were described in early investigations on co-condensation of atomic metals and acetylacetone and generalized in reviews.[16,41] Metal oxidation number and an amount of evolved molecular hydrogen depend on the synthesis conditions (in particular, on the presence of molecular oxygen and the velocity of metal evaporation) with yields of 10–32%.

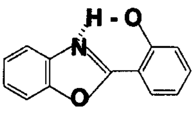
Later[60] a series of β-diketonates were obtained at 363–543 K (M = Co, Ni, Cu, Cr, Fe, Ti, Zr, Hf) with yields close to quantitative, 90–100%, using small metal particles instead of "metal atoms". In opinion of the author,[60] this method could be used for industrial production of β-diketonates. It was also noted,[60] that the productivity of this process sharply increases using an aerosol of ligands to introduce significant amounts of β-diketones into the reaction zone while regulating their concentration.

The cryosynthesis of coordination compounds, containing radionuclides, in particular, ^{63}Ni acetylacetonate were reported.[231]

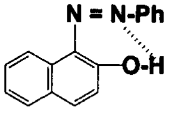
The feasibility of using cryosynthesis to obtain a wide variety of metal chelates with coordination MN_2O_2, was established.[232] Copper and nickel complexes of composition ML_2 are obtained from the chelating ligands (weak acids) **LIV–LVI**, where LH is the initial ligand system:



LIV



LV

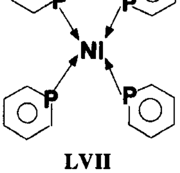


LVI

The yields of synthesized products are 10–60%; they were characterized by IR spectroscopy and X-ray diffraction. The complexes are generally identical to chelates prepared from the same ligands and metal salts. The main advantages of cryosynthesis of metal chelates, in comparison with conventional syntheses, are the following: (1) the time of the process is reduced to a few minutes, (2) no solvents are used, and (3) the products have the precise composition ML_n, whereas, starting from metal salts, the chelates ML_mX_n ($X = Hal^-, NO_3^-, CH_3COO^-$, *etc.*) could also be obtained.

5. CONCLUSIONS

This paper shows that cryosynthesis with metal atoms at low temperatures and "pure" gas-phase reactions without a condensed phase at high temperatures have possibilities for synthesis of various types of complexes, especially π-complexes of aromatic and cyclodiene ligands. The main advantages of this method are the following: it is possible (and frequently it is a unique way) to prepare metal π-complexes without solvent molecules or acidic radicals and the time of synthesis is reduced. Among the π-complexes, it is necessary to mention those with η^6-coordinated nitrogen-containing heterocycles,[183–185,233,234] which are impossible to obtain by conventional synthesis. In this respect we note that a series of heteroarene compounds ML_n ($L = \alpha,\alpha'$-bipy, C_5H_5P), obtained conventionally, could be attributed to π-complexes.[58,235] Thus, as a result of the interaction of *bis*-(1,5-cyclooctadiene)nickel with C_5H_5P, the coordination compound $(C_5H_5P)_4Ni$ was isolated, which is a σ-complex, according to X-ray diffraction data:[235]



LVII

The η^1-complexes of C_5H_5P with chromium $[(\eta^1\text{-}C_5H_5P)_6Cr]$ and iron $[(\eta^1\text{-}C_5H_5P)_5Fe]$ have also been described.[161] However, attempts to isolate similar compounds for pyridine were unsuccessful, although their formation in solution was established.[235]

Direct gas-phase synthesis gives extremely pure chemical substances. For example, synthesis of *bis*-ethylbenzenechromium by *Fisher*'s method leads to formation of homologs with different numbers of alkyl substituents; use of cryosynthesis produces an individual compound.[16] It is very important in the preparation of metal films or standard substances with constant characteristics: melting and boiling points, vapor pressure, viscosity, density, *etc.* Another recent important application of metal vapor chemistry[74] is the formation of intrazeolite metal clusters, where small metal clusters are deposited in the supercages of zeolite. Other detailed applications of the cryosynthesis are presented in the same monograph.[74]

However, this procedure has significant disadvantages in requiring special high vacuum equipment and in lower yields in comparison with conventional methods.

Unfortunately gas-phase synthesis using chelating ligands is very limited[236–239] and cryosynthesis of adducts of ligand systems having N, P, O, S-donor centers (L)[21,236] are practically absent. This is unusual since formation of adducts $MX_n \cdot mL$ is theoretically possible using metal, ligand and halogen vapors in these conditions. Perhaps, adducts of metal chelates could also be obtained, for example those of acetylacetonates with N-bases $M(acac)_2 \cdot mL$. However, dissociation of adducts is possible as *Lewis* acids (used to prepare adducts) in gas-phase conditions.

In our opinion, the gas phase is important for syntheses of compounds difficult to prepare by conventional chemical methods, and for complex-formation, where high yields of metal complexes could be expected.

Recent review articles and monographs on partial aspects of the cryosynthesis and related areas have been published.[19–21,25b,27,74,78,93,240–242,243] Study of reaction products using ion-cyclotron resonance have opened new possibilities (28,29,244 and references therein).

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