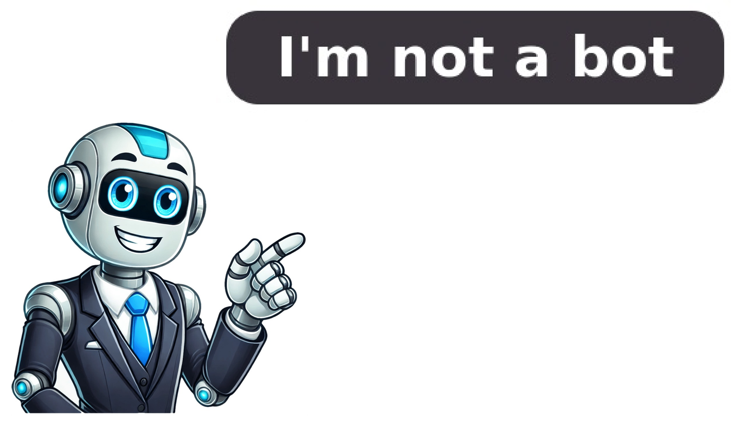
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1. Presented by :Arvind Singh Heer(M.Sc -Analytical Chemistry)Organometallic CompoundsOrganometallic Compounds 3. Organometallic CompoundsOrganometallic CompoundsThe 1st Zieses compound/salt (Sec. 13-1).The organic molecule is attached to the metal via the electrons ofthe ethylene ligand.Compounds with CONi(CO)4 Mond (purification of Ni).The Big Boom in Organometallic ChemistrySynthesis of ferrocene (Sec. 13-1).Began the era of modern organometallic chemistry. 4. Organic Ligands andOrganic Ligands andNomenclatureNomenclatureA number of ligands may bond through different number of atoms.The number is indicated by (eta) followed by a superscript.Ferrocene contains the pentahaptocyclopentadienyl ligand.hapto means to fastenDo a few others. 5. The 18-Electron RuleThe 18-Electron RuleTotal of 18 valence electrons on the central atom (thereare many exceptions). Table 13-1 (Sec. 13-3-1).Cr(CO)6(5-C5H5)Fe(CO)2Cl(CO)5Mn-Mn(CO)5(3-C5H5)(5-C5H5)Fe(CO)In general, hydrocarbon ligands come before the metal.HM(CO)5 The metal is in the 1strow. 6. The 18-Electron RuleThe 18-Electron Rule18 electrons represent a filled valence shell for atransition metal.Why do many complexes (if not most) violate the 18-electron rule?The 18-electron rule does not consider the type of bonding andinteractions. The interactions between the ligands and themetal need to be identified to determine if the complex willobey or violate the 18-electron rule. This treatment will alsoidentify why in many cases. 7. Interactions between theInteractions between theLigands and the MetalLigands and the MetalExamine the MO diagram for Cr(CO)6.This includes interactions between the d-orbitals and the -donor/-acceptor orbitals of the six ligands.Understand this diagram in terms and strengths of the different types ofinteractions.18-electron is the most stable for this type of complex.Assuming the d-orbitals to be at similar energy levels, which complexwould you predict to be the most stable?Complexes that possess ligands that are both strong donors and acceptors shouldbe the most likely to obey the 18-electron rule. 8. Interactions between theInteractions between theLigands and the MetalLigands and the MetalHow about ligands that have different donor and acceptorcharacteristics?Ethylenediamine is a donor, but not as strong as CO. Whyaffects does this have on the diagram studied previously?The [Zn(en)3]2+complex is stable. How many electrons? 9. Interactions between theInteractions between theLigands and the MetalLigands and the MetalHow about TiCl62-? It has 12 electrons. Can you justify thiswith an interaction diagram? 10. Interactions between theInteractions between theLigands and the MetalLigands and the MetalSquare-planar complexes (16-electron).Examine Figure 13-11 (Section 13-3-3).The ligand is a good donor and acceptor.Understand the interactions and influences on stabilization of thecomplex.The 16-electron square-planar complexes are mostlyencountered for d8metals.Oxidations states of +2 are common. 11. Ligands in OrganometallicLigands in OrganometallicChemistry Carbonyl ComplexesChemistry Carbonyl ComplexesExamine the frontier orbitals(HOMO and LUMO)Synergistic effect donor/ acceptorSpectroscopic evidence?Bond lengths are vibrationalfrequencies.Figure 5-14 12. Ligands in OrganometallicLigands in OrganometallicChemistry Carbonyl ComplexesChemistry Carbonyl ComplexesHow will the interaction diagram appear for a binaryoctahedral compound?HOMO These will have the same symmetry characteristics asa py orbital (previously).red(HOMO) A1g + Eg + T1uLUMO These will have the same symmetry characteristics asthe px and py orbitals (previously considered).red(LUMO) T1g + T2g + T1u + T2u 14. Bridging Modes of COBridging Modes of COCO can also form bridgesbetween two or moremetals.Position of C-O stretchingmode. Why is there a generaldecrease in frequency withincreasing metal centers? 15. Ligands in OrganometallicLigands in OrganometallicChemistry Carbonyl ComplexesChemistry Carbonyl ComplexesMost binary carbonyl complexes obey the 18-electron rule.Why?Why doesnt V(CO)6 form a dimer to obey the 18-electronrule?The tendency of CO to bridge transition metals decreasesgoing down the periodic table. Why?No synthesis discussion. 16. Ligands in OrganometallicLigands in OrganometallicChemistry Carbonyl ComplexesChemistry Carbonyl ComplexesOxygen-bonded carbonylsOccasionally, CO bondsthrough the oxygen atom inaddition to the carbon atom.Attachment of a Lewis acid tothe oxygen weakens the CObond. 17. Ligands Similar to COLigands Similar to COCS, CSe, CN-, and N2CN-is able to bond readily to metals having higher oxidationstates.CN- is a good donor, but a weaker acceptor (cannot stabilizemetals of low oxidation state).No NO complexes. 18. Hydride and DihydrogenHydride and DihydrogenComplexesComplexesHydride complexes (e.g. [ReH9]2-)Only a 1s orbital of suitable energy for bondingMust be a interaction (minimal basis set)Co2(CO)8 + H2 2HCo(CO)4Dihydrogen complexesZieses saltWhat are the types of possible interactions? What happens tothe H-H bond? Extreme case? 19. Ligands Having ExtendedLigands Having Extended SystemsSystemsLinear systemsEthylene, allyl, and 1,3-butadieneCyclic systemsC3H3, C4H4, and Figure 13-22. 20. Bonding InvolvingBonding Involving SystemsSystemsBonding between ethylene and a metal. donation/ acceptanceIf orbitals of appropriate symmetry are present (isolobal), aninteraction may occur (Fig. 13-23).Construct an MO diagram.-allyl systems (trihapto ligand)Examine Fig. 13-25, could construct MO interaction diagram.[Mn(CO)5]-+ C3H5Cl (1-C3H5)Mn(CO)5 (3-C3H5)Mn(CO)4 + CO 21. CyclicCyclic SystemsSystemsC5H5 (1, 3, or 5bonding modes (4can also beobserved)).Ferrocene (5-C5H5)2FeOrbitals on the ligands and metal can interact if they have thesame symmetry.Strongest interaction is between orbitals of similar energies.What is the point group?Lets give it the treatment!! 23. Fullerene Complexes (anFullerene Complexes (animmenseimmense system)system)Adducts to the oxygens of oxmium tetroxideC60(OsO4)(4-t-butylpyridine)2Complexes in which the fullerene itself behaves as a ligandFe(CO)4(2-C60), Mo(5-C5H5)2(2-C60)Compounds containing encapsulated metalsUC60, Sc3C82 24. Fullerenes as LigandsFullerenes as LigandsC60 behaves primarily as an electron deficient alkene. Bonds tometals in a dihapto fashion through a C-C bond at the fusion of two6-membered rings (Fig. 13-35).[(C6H5)3P]2Pt(2-C2H4)+C60[(C6H5)3P]2Pt(2-C60)What affect does this have on the two carbon atoms? 28. Alkyl Complexes (M-C)Alkyl Complexes (M-C)Grignard reagents (Mg-alkyl bonds) and methyl lithium.Grignard reagents can be used to synthesize organometalliccompounds containing an alkyl groupThe interaction is largely through donation.Metals containing only alkyl ligands are rare and usually unstable. 29. Carbene Complexes (M=C)Carbene Complexes (M=C)Fisher-type and Schrock-type complexes.What are the differences between the two different type of carbenecomplexes (Table 13-6). 30. Carbene Complexes (M=C)Carbene Complexes (M=C)Bonding in Fisher carbene complexes. donation and back bonding (illustrate).Complex is generally more stable if the carbene atom isattached to a highly electronegative atom. The electronegativeatom participates in the bonding.Similar to a -allyl system (illustrate, Fig. 13-41).Can be represented as a hybrid structure.What type of spectroscopic evidence would show the existence ofM=C? 31. Carbene Complexes (M=C)Carbene Complexes (M=C)Discuss the proton NMR of Cr(CO)5[C(OCH3)C6H5].At high temperatures there is one signal from the methylprotons and at low temperatures there is one signal. Why? 33. Spectra Analysis andSpectra Analysis andCharacterization of OrganometallicCharacterization of OrganometallicCompoundsCompoundsX-ray crystallographyInfrared spectroscopyNMR spectroscopyMass spectrometryElemental analysisOthers 34. Infrared (IR) SpectraInfrared (IR) SpectraThe number of IR bands depends on the molecular symmetry (IRactive modes).Monocarbonyl complexesDicarbonyl complexesLinear and bentThree or more carbonyl on the complex (Table 13-7).We will assume that all the IR active modes are visible and distinguishable.Exercise caution when using this table. 35. Positions of IR BandsPositions of IR BandsTerminal > doubly bridging > triply bridgingWhy?As -acceptor ability increases, the C-O stretch decreases.What may affect the ability to accept electron density into the -acceptor orbitals? 36. NMR SpectraNMR SpectraChemical shifts, splitting patterns, and couplingconstants are useful in characterizing environments ofatoms.13C NMRTable 13-9 (unique carbon environments)1H NMRProtons bonded to metals are strongly shielded (chemicalshifts)Table 3-10Ring whizzingUsing spectroscopy for identification. 38. ReferencesReferences1. Organometallic Chemistry and Catalysis, Didier Astruc2. Organometallic Chemistry, R.C. Mehrotra3. Inorganic Chemistry: Principles of Structure and Reactivity, JamesE. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi4. Reaction Mechanisms of Inorganic and Organometallic Systems,Robert B. Jordan; Professor of Chemistry, University of Alberta5. rmv/ch102/ic6.pdf-ThankYou 1. Organometallic chemistryB. Sc. III ChemistryDr. S. H.Burungale 2. IntroductionOrganometallic compounds have many applications in industrialand synthetic organic chemistry. They are widely used as catalyst orintermediate for several major synthesis .The term organometallicwas first introduced by E.C. Frankland. He was working on organarsenic compounds and first synthesized organomercury in 1848.The use of organometallic compounds in the manufacture ofagrochemiclas,pharmaceuticals, semiconductors, Flavours,Fragrances and ceramic applications .Thus the study oforganometallic compounds become essential today to day life. 3. DefinitionA compounds which contains at least onemetalcarbon bond is known as organ metallic compound.Eg.Li(CH3)4, Be(C5H5)2, Al(CH3)6 etc.The electronegativity of metals are less than carbons. i.emetals are more electropositive than carbon.Most of the metals are of main group elements orTransition metals or lanthanides and actinides arebonded to carbon cataining ligands susch as alkyl,alkene, aryl groups. 4. Classification of OMc1. Ionic Organometallic Compoundsa. Most of the alkali and alkaline earth metals.b. Soluble in polar solvents.c.Short life periods.d. Maximum ionic character2. Covalent containing metal carbon sigma bonds.The organometallic compounds of group II Zn,Cd,HgThe electronegativity of of these metals are low as compared alkali and alkalineearth metals .therefore partially potive charge on metals and partially negativecharge on ligads.3. Organometallic compounds containing Pi ligands.The organometallic compounds of alkene , alkynes and other carbon containingcompounds having electrons in their pi molecular orbitals. 5. Nomenclature of Organometalliccompounds1.Organometallic compounds of s block elements are named assubstituent names used in organic chemistryEg. Li4(CH4)4 --------- tetra methyl lithium2. Organometallic compounds having ionic character . Na[C10H8]Sodium naphthalide.3. Organometallic compounds of p block named asB(CH3)3 trimethyl boron4.In determining oxidation state of a metal ion in organometalliccompounds.Eg. Diphenyl mercury. 6. SYSTEM OF NOMENCLATUREThree general types of nomenclature.1. Binary Type Nomenclature:Used to name salt like ionic species.OMC of ionic character are considered as derivatives of inorganicsalts..e.g. CH3Mg+Br- : methylmagnesium (II) bromide.C6H5Hg+OOCCH3- : phenylmercury(II) acetate.(CH3)3Sn+Br- : trimethyltin (IV) bromide.The usual rules for naming the substituents are usede.g.(C6H2Cl3)2Hg : bis(trichlorophenyl) mercury. 7. 2. Substitution Nomenclature:OMC of the main-group elements are similarities to organiccompounds.Therefore, organic nomenclature rules can be used.They are named by first naming the organic group with proper endingfollowed by name of metal.The s and p-Block organometallics are named either asi) derivatives of hydride orii) ii) substituents in organic compounds.i) As Derivatives of Hydride:The first system is based on the concept of a parent hydridee.g. SiH4 = silane, AsH3 = arsaneetc.The OMC are considered as the derivatives of parent hydrides formedby replacement of H. (used for naming p-block element compounds)B(CH3)3 Trimethylborane, Si(CH3)4 Tetramethylsilane,As(C2H5)3 triethylarsane, B(C6H11)2H -dicyclohexylborane. 8. ii) As Substituents in Organic Compounds:The name of OMC is derived from organic group attached via acarbon. Bonds are highly covalentThe ending e of the parent organic species is changed to ylfollowed by the name of metal without any gap.For normal chain, the locant 1 is omitted, for branched chain; the locantnumber including 1 must be cited.For example:CH3- CH2- CH2- CH2- CH2- Na : Pentanylsodium.*This method is used to name covt OMC having saturated, acyclic andmonocyclic hydrocarbon substituent groups.e.g. BuLi : Butyllithium,CH3Na : Methylsodium,CH3 CH2Li : Ethyllithium,CH2=CHCH2Na : 2-Propenylsodium,CH2=CHNa : Ethylenesodium, 9. 3. Co-ordination Nomenclature (For OMC of d- and f-block elements) OMC are thought to be produced by additionreactions therefore, It name is built accordingto co-ordination chemistry rules. The OMC containing an organic ligand arenamed by replacing final e of parentcompounds by ide. E.g. CH3 methanide, C5H5 cyclopentadienide. Names of Neutral and cationic names are notmodified. 10. , k Notations:x5-Cp 3-Cp 3-allyl 1-allylM MMMTo designate the points of attachment of ligands to metal(s), the and -notations are used. eta notation*The numbers of C-M bonds are specified by prefix (eta), called hapticity.If the ligand bonds through one atom, it is called monohapto. Some ligands,e.g. benzene, may bond to M through 1, 2 or 3 bonds. So, we can describebenzene as bi-, tetra- or hexa-hapto and use the notation 2, 4 and 6,C6H6)2Cr : bis(6-benzene)chromium.For example 11. 2. The (mu) Notation:*Organic species that bridge two M are indicated by prefix (mu),which appears before ligand and separated by a hyphen.If bridging ligand is complex, it is enclosed in bracket. For example: (-ethane-1,1-diyl)bis(pentacarbonylrhenium)3. The k (kappa) Notation:*The points of attachment (ligation) of a polyatomic ligand to M areindicated by the italic element symbol preceded by k (kappa)*Metal-Metal bonding may be indicated in names by italicized atomicsymbols of the appropriate metal atoms, separated by a long dash andenclosed in parentheses. 12. Coordination geometries17CN Geometry Example2 linear3, trigonal3, T shape4, tetrahedron4, square planarLL M LL[NCAgCN]Pt(PPh3)3[Rh(PPh3)3]+Ti(CH2Ph)4Cl H HCl PtClH H 15. Preparation of organometalliccompounds 16. Synthesis and structural study ofAlkyl or aryl compounds of Be and Al1. Transmetallation :Alkyl or aryl beryllium are prepared by heatingpure beryllium metal with mercury alkyl oraryl.a. Be + HgR2 BeR2 +Hgwhere R= CH3,C2H5 groupsBe + Hg(CH3)2 Be(CH3)2 +HgEther 17. GENERAL:OMCs are similar to H- compounds (similar elect-ve of M-C, C-H & M-H)21*The species that lose H form ionic compounds with alkali metals.OMCs are used in organic synthesis.They are superior to Grignard reagents (e.g. in alkene polymerization).*They are liquids or low melting solids, thermally stable than other OMCof the same group. Soluble in organic and non-polar solvents. All OMCsof alkali metals are unstable.*In alkaline earth metals, the reactivity and electropositivity in thegroup. Therefore, the OMC of Be and Mg are covalent, while Ca, Sr andBa form only few ionic compds that are unstable and of little utility.*OMCs of group 13 elements exist as electron deficient species having+3 OS (e.g.Al3+), with 3c-2e bonding.Organoaluminium compounds are used for alkene polymerization,catalysts& chemical intermediates.Trialkylaluminum is a diamer but often written as the monomer, AlR3. 18. i) Reaction of Alkyl or Aryl Halide with Li Metal:Alkyl/Aryl halides react with lithium in inert solvent such as ether,benzene, petroleum ether, cyclohexane etc.The moisture and air must be excluded as they react with reactant andproducts.A) Organolithium Compoudsether4R X + 8Li 4R Li + 4 LiX350CEt2OBr+ 2LiBromobenzene PhenyllithiumLi +LiCl1.2. 19. 4CH3Cl + 8Lisolvent (CH3Li)4 OR (CH3)4Li4 + 4LiClC2H5Li +2LiClExamples3.4. C2H5Cl+2LiC6H5Li+ 2LiCl-100CEt2OCH3CH2CH2CH2Cl +2LiButyl chlorideCH3CH2CH2CH2Li + LiClButyllithium5. C6H5Br+2Li6. 20. Features:*The organolithiums react slowly with ether, therefore, thesynthesis is usually carried out in inert atmosphere ofnitrogen or argon at low temperature.*The use of cyclohexane as solvent, alkyl or arylchlorides over bromides and iodides minimizes thepossibility of side reactions*The yield and reactivity is improved by adding 0.5-1% Na. 21. Alkyl and aryl lithium can be synthesized by reacting the Organiccompounds with alkyl/ n-butyl lithium, ((C4H9)Li called nBuLi).The reaction, in general, can be written as;ii) Metal Hydrogen Exchange (Metallation):2.RH+R'Li RLi+R'H2 6 4 9C H + (C H) Li C H Li + C H2 5 4 101.Ethane ButylLithium Ethyllithium Butane+CH3Li C5H5Li + CH4O +PhLiOLi+C6H63.4. 22. The reactions gives small aggregates having multi-center bonding;e.g. (CH3)4Li4 or (C2H5)6Li6which contain bridging alkyl groups*When ethers are solvent, methyl lithium exists as(CH3)4Li4.*while in hydrocarbon solvents (e.g THF), it exist as(CH3)6Li6.*LiCl destroys (CH3)4Li4, so, LiCl is added in reaction. 23. iii) M-X Exchange (Metathesis/ Double Displacement):Double displacement reaction betn OMC (MR) &organohalide, (RX) involves M-X exchange therefore, it iscalled metal-halogen exchange or metathesis.A large number of OMC are prepared in thisway.The common reagents used are;alkyllithium,alkylmagnesium andalkylaluminium.lithiumButyllithium is most suitable for preparingderivatives of comparatively acidic hydrocarbons.This type of reaction can be represented as;RX + MR RM + RX 24. Examples+ C6H5 LiCH3+ C6H6CH2LiN N1.4 9Phenyl iodide Butyllithium Phenyllithium Butyl iodideetherI + (C H) Li Li + C4H9I2.3. 25. iv) Transmetallation:One OMC react with other, the exchange of organic part takesplacebetween them, such reaction is called transmetallationreaction.These reactions are most convenient to prepare vinyl, allyl andunsaturated derivatives.PhLi + (CH2=CH)4Sn4 CH2=CHLi+ Ph4SnLithium alkyls can also be prepared by metal displacement reaction.Usually organomercury compounds are used when the isolation of theproduct is required.For example:R2/Ar2Hg + 2Li 2R/ArLi + Hg(CH3)2Hg + 2Li 2CH3Li + HgOrganolithium compounds are mainly used in homogeneous catalysis,for example, in stereospecific polymerization of alkene 26. i) Metathesis:Beryllium halide reacts with an OMC of a different metal(e.g.lithium,sodium etc.).etherBe(CH3)2 + 2LiCl (Dimethylberyllium)(CH3)2Be + 2 MgCl2etheretherBeCl2 + 2 CH3LiBeCl2 + 2 MgCH3ClBeCl2+ 2 C6H5Li Be(C6H5)2 + 2LiCl (Diphenylberyllium)B)ORGANOBERYLLIUM3(C2H5)2Be + 2(C6H5)3B 2(C2H5)3B+ 3(C6H5)2BeDiphenylberylliumBeCl2 reacts with Na[C5H5]2 to give Bis(cyclopentadienyl)Be (doubledisplacement). The anion is transferred to less electropositive Be(II).BeCl2 + 2 Na [C5H5] [C5H5]2Be + 2NaClBeryllium is less electro+ (or more electro-) than Li, Na, Mg, so it formsOMC while more electropositive metal forms halide.However, the product is always associated with ether molecules whichcan not be separated easily. 27. ii) Transmetallation fromMercury Alkyl:This method is used to get ether free product.Pure Be is heated with mercury alkyl or aryl.1100CBe + (CH3)2HgBe + (C6H5)2Hg (CH3)2Be + Hg (C6H5)2Be + HgThe product is collected by vaccum distillation.OMCs of Be are toxic, have no commercialapplications.They are used in laboratory as syntheticintermediates. 29. The reaction of Al &chloromethane gives Dimethylaluminium, (CH3)4Al2Cl2.This is then reduced with sodium to give (CH3)6Al2.ii) Reaction of alkyl halidewith Al metal:(CH3)3Al2Cl3 disproportionate to (CH3)4Al2Cl2 and(CH3)2Al2Cl4.NaCl is added to remove (CH3)2Al2Cl4 as soluble Na[CH3AlCl3] then(CH3)4Al2Cl2 is separated by distillation. It is then reacted with NaThe commercial synthesis of triethylaluminium is carried using Al &alkene and H2gas at 1100C temp. under pressure (hydroalumination)This route is relatively cost effective. 30. iii) From Alkyl Aluminium Hydride:Aluminium hydride reacts with olefins to give aluminium alkylsAlH3 + 3 CH2=CH2 (CH2CH3)3AlThe reaction is specific to Al hydrides.Aluminium hydrides are made by reaction of Al, H2 andaluminium alkyls.Organoaluminium compounds are used as Zeigler Nattacatalyst for alkene polymerisation & in aluminium alkoxides &amides making. 31. STRUCTURAL STUDY OFALKYL LITHIUM:1. They are crystalline & polymers (in liq &sol state)2. They are Covalent3. OMC of Li are tetramer & hexamer.4. The alkyl compounds are electron deficient.5. The synthesis always gives some quantity ofaggregates having multi-centre bonding & bridgingalkyl groups e.g. (CH3)4Li4 & (C2H5)6Li6.6. The tendency of aggregation decreases withincreasing bulkiness of organic groups.7. The monomeric do not satisfy octate rule, therefore,they form aggregates where e- are delocalized inmulti-centered bonds. 32. 8. XRD study indicates presence of 4 Li at the corners of atetrahedron (td).Each of CH3 lies above middle of each td face & forms a triplebridge to the 3 Li atoms which make up the face of Td(distorted cube)Unit cell showing distorted cubic structure of Li4(CH3)4 unit. 33. 9. Each C in (CH3)4Li4 unit is bonded with adjacent Li4tetrahedra providing a sort of linking throughout thesolid lattice.Thus, a number of (CH3)4Li4 units are interconnectedalong cube diagonals via CH3 bridging groups asshow below; 34. 10. In (CH3)4Li4, each Li has 3 adjacent C atoms & eachC atom has 3 Li and 3 H atoms as nearestneighbours.Li- C length within tetrahedron is 231 pm.The Li- C in adjescent tetrahedron is, however, littlehigher (236 pm).It has 12 Li-C links with only 8 e- to hold themindicating that compound is electron deficient.C has CN = 7 (it is bonded to 3 H, 3 Li in onetetrahedron and 1 Li in the adjacent tetrahedron).Li also has CN = 7 (since it is bonded to 3 Li atoms,3 methyl C in a tetrahedron and 1 Li in anothertetrahedron). 35. 9. The CN = 7 cannot be explained as the C atom has only one sand three p orbitals available for bonding.It can be explained on the basis of formation of four centered-two electron (4c-2e) bonds.The bond is formed by overlap of sp3 HO of C and s type AO ofeach of the 3 Li atoms. The bond has two electrons and islocalized over four centers (Li3C).This 4c-2e bond is present over each face of Li4 tetrahedra.Localized 4 centered MOs pointing towards centre of Li3C 36. 11.According to MOT, 4c-2ebonding is explained byformation of a set ofsemilocalized MOsTotally symmetric combinationsof one sp3 HO of C and three stype AO from 3 Li gives fourMOs.Out of 4 MOs one is bonding,two are nonbonding and one isantibonding.The lowest energy MO (bonding)occupies two electrons (onefrom C & one from Li) whileother MOs are empty. 37. 2. STRUCTURAL STUDY OF ALKYLBERYLLIUM:Be(4): 1S2,2S2,2P0(GS), 1S2,2S1,2P1(ES),So it has two electron for bonding.C has only one electron in SP3 HO.So to bind two CH3 and one Be we need fourelectons. Therefore,Alkylberyllium compounds are electron deficient.2. Methylberyllium, is a monomer in vapour phase. Insolid state, it exists as polymer.3. Bulkier alkyl groups attached to Be atom showlower degree of polymerisation.4. XRD studies indicated polymeric structure withtetrahedral Be co-ordinated by methyl groups.5. The structure of (CH3)2Be is analogous to BeCl2.6. The bonding in Be(CH3)2 is 3c-2e bonds(Analogous compound BeCl2 has 2c-2e bonding) 38. 7. The 3c-2e bonding:In Be(CH3)2 , both, Be and C are sp3 hybridized.Be(4) : 1s2, 2s2(G.S)Be(4) : 1s2, 2s1,2p1 (E.S) [sp3 hybridization]C(6) :1s2, 2s2,2p2.(G.S)C(6):1s2, 2s1,2p3.(E.S) [sp3 hybridization]In Be, one s orbital (with one electron) and three p orbitals(withone electron) hybridize to produce 4sp3 HOs containing twoelectrons.In this way only two HOs contain unpaired electrons,whileother two HOs are empty.The C HOWEVER forms 4 HOs containing four unpairedelectrons. 39. It has 2 bridging CH3 groupslinking 2 adjacent Be atoms by3c-2e bonds. The overlap of 1sp3 HO(empty) offirst Be, 1sp3 HO of C (from CH3)containing 1 electron and sp3 HOof another Be containing 1electron give 3c-2e bonding. Similarly, other 3c-2e bond isformed. The overlap of 1sp3 HOof first Be containing 1 electron,1sp3 HO of C from other methylgroup containing 1 electron andan empty sp3 HO of other Be. The bonding pair of electron isdelocalized over three centers.Each C atom in Me2Be shows aCN = 5. 40. Simple methyl beryllium is polymeric However,higher alkyls are progressively less polymerized. E.g, diethyl and isopropyl beryllium are dimeric,while t- butyl beryllium is monomeric.Polymeric structure of M(Me)2, M = Be, Mg. 41. STRUCTURAL STUDY OFALKYLALUMINIUM1.Tri alkyls & aryls of Al are dimers (in solid & vapourphase) with terminal and bridging methyl/ arylgroups.2. (Me3Al)2 is a solid (mp 150C) with methyl bridginginvolving 3c bonding (similar to AlCl3,with methylgroups replacing Cl atoms).3. In AlCl3, the bridging AlClAl bonds are normal 2c-2e bonds While in alkylaluminium compounds, theAlCAl bonds are 3c- 2e bonds & are longer thanthe terminal Al-C bonds, 42. 4. 3C bonding involves sp3 hybrid orbital from two Alatoms and bridging alkyl carbon atoms.Al(13) : 1s2, 2s2, 2p6,3s1,3p2 (E.S)sp3 hybridization.C(6) : 1s2, 2s1,2p3. (E.S)sp3 hybridization.The hybridization on both Al and C is sp3. Out of 4HOs on Al, one is empty. This empty HO of one Al,half filled HO of other Al and half filled HO of onemethyl C overlap to produce one bridge bondinvolving 3c-2e.Similarly, second bridge is produced by overlap ofone half filled HO of first Al, empty HO of other Aland half filled HO of second methyl C. 43. Though R is bulkier, stillthe compound exists asdimer5. Triphenyl aluminium exists as a dimer with bridging phenyl groupsThis structure has less steric hindrance. The 3c-2e bonding isstrengthened due to participation of phenyl pi orbital.6. Steric factors also have a powerful effect on the structures ofaluminium alkyls. For example, triphenyl aluminium is a dimer but themesityl, (2,4,6-(CH3)3C6H2)3Al compound is a monomer. 44. 7.NMR study of Me6Al2At 250C shows 1 resonance peak.However, when spectrum is taken at -750C, it shows 2resonance peaks.The two lines corresponding to presence of 2 types of H envt.One due to bridging and other due to terminal Me groups.This means at RT, two types of alkyl groups (bridging andterminal) are interchanged rapidly giving only one peak.This kind of rapid exchange of alkyl groups provides a facilemechanism for alkyl exchange reactions. 45. MONONUCLEAR CARBONYLDefinition:Compounds of Transition metals with carbonmonoxide are termed as metal carbonyls orsimply carbonyls.The general formula is Mx(CO)y. M transitionelement.The metal atom act as Lewis acidwhile CO act as Lewis base (ligand).When x is 1,2,3 etc. then they are calledmononuclear, binuclear or trinuclear carbonylsrespectively.The elements from groups 8,9 and 10 form manycarbonyls. In carbonyl metal is, 46. The important features are;1) CO is not a strong ligand still it forms a strongbond with M.2) M are always in lower OS, (zero & low positive ornegative OS.3) Almost all carbonyls obey 18 valence electronrule.4) All carbonyl compounds are volatile and toxic.The toxicity is dueto strong, irreversible bondingwith Hb in blood.5) The transition metal organometallic compounds arevery similar to many of the co-ordinationcompounds in physical and chemical properties.6) In fact, the properties of organometallics aremuch more organic in nature. 49. The 18 electron rule (EAN)It states that thermodynamically stable organo-metallics hasthe sum of the metal d electrons plus the electronsdonated by the ligands is equal to 18.The central metal ion can accommodate electrons in d, s, andp orbitals, giving a max. of 18.In this way, the metal attains electron configuration of thenext higher noble gas.The 18-electron rule is also known as the noble-gas rule orthe effective atomic number (EAN) rule.Complexes with 18e counts are referred as saturated,because they have no empty low-lying orbitals to whichanother incoming ligand can bind. Complexes with countslower than 18e are called unsaturated and canelectronically bind additional ligands. 50. The 18-e Rules:Counting of electrons:The rule is used to predict the existence & number of metal-metal bonds. Most stable OMC obey the rule.CO supplies 2 electrons to metal.The intramolecular partitioning of electrons has to ensure thatthe total complex charge remains unchanged.A metal-metal bond, if present, contributes one electron tothe count on each metal. Metal-metal double or triple bondssupply 2 & 3 electrons, respectively, to each metal.The electron pair of a bridging ligand such as CO donates oneelectron to each of the bridged metals 51. However other stable compounds with electron otherthan 18 do exist.In such compounds, the factors such as CFSE, nature M-C ofbonding affects the stability of the compound.Some of the organometallic compounds of d block(Groups 9& 10) obey 16-e- rule.V(CO)6 have 17 e-, therefore called 17e- species. It readilycompletes 18-e- configuration by accepting an electron fromreducing agent or by dimerising with another molecule.For example, Mn(CO)5 has 17-electrons. Two moleculesshare their odd electron, in order to form a Mn-Mn bond.Consequently each Mn becomes an 18- e-species. 52. A simple exampleFe FeCOOC CCOCOOCOCCOOC3 CO -- 6e-3 CO -- 3e-Fe -- 8 e-Fe-Fe -- 1 e---------18 e-OCOTetracarbonyl nickel(0), Ni(CO)4.[28(Ni) + 2 X 4 (CO) = 36 (Kr)]Pentacarbonyl iron(0), Fe(CO)5.[26(Fe) + 2 X 5(CO) = 36 (Kr)] 53. Bonding in Metal Carbonyls1. Spectroscopic study indicated that CO, is present as a part of themolecule.2. Simple carbonyl contains terminal CO groups which bondsthrough C and not O. However, polynuclear carbonyls maycontain bridging CO.3. In carbonyls, the sigma bonding is reinforced by additional pibonding which stabilizesi) complexes & ii) very low oxidation states of metal.4. Many carbonyl compounds have metal in a zero oxidation state.2. The very low oxidation states are not found with sigma-bondingligands such as H2O & NH3.5. In CO, the highest energy occupied molecular orbital (HOMO) is asigma 2p orbital & lowest energy unoccupied molecular orbitals(LUMOs) are the pi 2p antibonding orbitals. 54. Bonding in Metal Carbonyls6. 6 CO ligands are simultaneously donating electrons toa Metal via the overlap of the HOMO of CO with anempty d or hybrid orbital of the M.This leads to formation of bond between M and COi.e. (MCO).7. However by this, electron density on the metal ionbecomes very high. To stabilize low oxidation statesexcess electron density is to be removed, this is doneby another type simultaneous bonding with CO. Thissimultaneous bonding called back bonding 55. A filled d orbital on the metal overlap with the pi LUMO of thecarbon monoxide. These two orbitals have the correct symmetryfor overlap.This removes the electron density from the metalcenter, back onto the carbonyl ligand to some extent (MCp).This additional bond is a dp bond.So, the carbon monoxide is said to be a sigma-donor and pi-acceptor and the metal is a sigma-acceptor and pi-donor.Thus the electrons flows from carbon monoxide to metal throughthe bonding and a flow through the bonding in the reversedirection. This interaction is known as back bonding or synergisticbonding.This synergistic effect leads to a strong, short, almostdouble, covalent bond between metal and carbon atoms. 56. Synergic Bonding: Back bondinge.g. Ni(CO)4], [Fe(CO)5], [Cr(CO)6],[Mn2(CO)10], [Co2(CO)8], Na2[Fe(CO)4],Na[Mn(CO)5] 57. O C M orbital serves as a very weak donor to a metal atomO C M O C MCO-M sigma bond M to CO pi back bonding 58. Structure of some Metal-Carbonyls Electron diffraction studies indicated that in; Ni(CO)4 is tetrahedral (sp3 hybridn.) Cr(CO)6, Mo(CO)6, W(CO)6 are octahedral (d2sp3) Fe(CO)5 has trigonal bipyramidal(dsp3) CO ligand in each case force two s electrons to pairup in d orbitals. 59. a). For Ni(CO)4:Ni(28) : 1s2, 2s2, 2p6, 3s2, 3p6, 3d8,4s2 (G.S)Ni(28) : 3d10, 4s0 (E.S)sp3 hybridization (Tetrahedral)b) For Mo(CO)6 :Mo(42): 1s2, 2s2, 2p6, 3s2, 3p6, 3d10,4s2,4p6, 4d4,5s2 (G.S)Mo(42) : 4d6,5s0 (E.S)d2sp3 hybridization (octahedral)c)For Fe(CO)5 :Fe(26): 1s2, 2s2, 2p6, 3s2, 3p6, 3d6,4s2 (G.S)Fe(26) : 3d8,4s0 (E.S)dsp3 hybridization (tbp) 60. StructureNi Mo FeCOCOCOCOCOOCOCOCCOCOCOCO OCOCaCOb c Paul Brunel, Chlo Lhardy, Sonia Mallet-Ladeira, Julien Monot, Blanca Martin-Vaca, Didier Bourissou, Palladium pincer complexes featuring an unsymmetrical SCN indene-based ligand with a hemilabile pyridine sidearm , Dalton Trans., 2019, 48, 9801-9806.Kori A. Andrea, Tyler R. Brown, Jennifer N. Murphy, Dakshita Jagota, Declan McKearney, Christopher M. Kozak, Francesca M. 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Hall, Marcetta Y. Darensbourg, Regioselectivity in Ligand Substitution Reactions on Diiron Complexes Governed by Nucleophilic and Electrophilic Ligand Properties, Inorg. Chem. 2015 5 47, 3523-3535. Organometallic Compounds An organo metal compound is generally defined as one that possess a metal-carbon bond. The bond is between carbon of one or more alkyl groups or an organic group or molecule and a metal atom. The organic group may be any alkyl radical or a carbon atom in a molecule. But some non-metal atoms less electronegative than that of carbon can form a direct bond with carbon. For example B, As, P and Si elements can form bonds directly with carbon and but these are not organo metallic compounds. The organo metallic linkage can be represented as In some organic compounds the metal atoms are linked to oxygen instead of carbon atom. For Example acetates (derivatives of carboxylic acids) alkoxides (derivatives of alcohols) etc. These are not organo metallic compounds. (C3 H7 O)4 Ti; B(OCH3)3 also are not organometallic compounds because their structures are as follows. Some compounds in which though C-M bonds are present are not included in organo metallic compounds. For example metal carbides (Ex. CaC2) metal cyanides (NaCN): metal carbonyls {Ex: Ni(CO)4 }. The reason for this is the properties of such compounds are similar to those of inorganic compounds. Nomenclature In naming these compounds the name of the metal atom followed by the name of the alkyl or aryl group. But the number of alkyl groups of the same kind bonded to the metal atom is clarified by a prefix to the name of the alkyl group. Ex : H3 C Li Methyl Lithium H3 C-Zn-CH3 Dimethyl Zinc (H3 C)4 Pb Tetramethyl lead The organometallic compounds may contain H-atoms beside the alkyl groups . Ex (CH3)3 SnH. The organo metallic compounds are generally divided into two types. i) Symmetrical or normal - Ex: (C2 H5)4 Pb and. In these compounds, all the alkyl groups are same. Example: (C2 H5)4 Pb (CH3)2 Hg. ii) Mixed types - This type of compounds have different alkyl groups. Some of these mixed organo metallic compounds may contain other than hydrogen atoms also. Ex: (C2 H5)4 Hg (C4 H9)2Ch3, CH3 MgBr; (C4 H9)2 SnCl2, (CH3)3 SnH However all the bonds in the compounds need not be metal carbon bonds. Atleast one metal- carbon is sufficient to be called organo metallic compounds. Types of Organometallic compounds Nature of Bonds The organometallic compounds are classified into 4 types depending upon the nature of the bond formed between the metal and the carbon atom of the organic group. Ionic organometallic compounds - bonded covalent organometallic compounds -bonded covalent organometallic compounds Alkyl bridged organometallic compoundsI. Ionic organometallic compounds Highly electropositive metals form ionic organometallic compounds. In these compounds the metal is a cation is bonded to the hydrocarbon as the carbanion by non-directional electrostatic forces. Highly electropositive elements like alkali and alkaline earth metals form this kind of a bond . R - M+ for Group1 and R 2 M2+for Group II Ex : (C6 H5)3 C- Na ; (C5 H5)2 Ca+, (C5 H5)2Na Preparation Cyclopentadienyl sodium is prepared by the reaction of cyclopentadiene with sodium, in an inert solvent like kerosene, benzene + 2 Na Na + H2 , 2Na + 2 C5H6 2 NaC5H5 + H2 Properties Colourless salt like solids Are electrolyted when fused Insoluble in non-polar solvents Hydrolysed by water to liberate hydrocarbon Stability It depends on the stability of organic anion. Compounds containing stable anions are highly reactive. The ionic nature of bond increases with increasing difference in electronegativity. Ionic character increases more negative if it is a part of unsaturated group and further negative if substituents like X, N or O are present- bonded covalent organometallic compounds Covalent bond formed between metal and the carbon atom of an organic group. This kind of bond is formed by metals with low electropositive nature. Nonmetal atoms and weakly electropositive metal atoms form this type of compounds. A metal atom and a carbon atom share a pair of electrons forming a - bond in these compounds. Ex: (CH3)3 Sn Cl; (C H3)2 Si Cl2; (C2 H5)4 Pb; (CH3)2 Zn. The polarity of the C-M bond depends on the difference between the electronegativities between the carbon and the metal. The stability of the bond depends on the nature of the alkyl group linked to the metal and the other groups bonded with M. --SiCl3 Trichlorocyclopentadienyl siliconIII. - bonded covalent organometallic compounds Transition metal atoms only generally form -bonded compounds. Ferrocene, an ionic compound, was the first compound of this type. Two C5 H5 rings are enclosing the iron atom. This is a sandwich compound. In this compound all the Fe-C distances are identical. The ring structure is symmetric about the metal atom. The -electrons of cyclopentadienyl anion overlap the vacant d-orbitals of the metal and form -bonds. As a consequence these compounds are known as - bonded compounds. Ethylene, acetylene, dienes like butadiene, aromatic molecules give these compoundsIV. Bridged Organometallic compounds Two metal atoms are bridged by alkyl groups . Bridging groups have 2 e 3 c bonds. Some of the examples for this type of compounds are Dimerictrialkylaluminium (AIR3)2 Polymeric dimethylberyllium [Be (CH3)2]n, Polymeric diethyl magnesium [C2 H5)2 Mg]n These compounds exist as either dimeric or polymeric substances. The M-C bonds in the bridge groups have identical bond lengths. All bonds can not be considered as 2 electron , 2 centre covalent bonds; bridge bonds are 2e 3c bonds.2. Organometallic compounds 3. Organometallic compounds: Classification 4. Organometallic compounds: Classification 5. Organometallic compounds: Classification 8. On the basis of 18 VE systemClass 1: 12-22 electrons With sigma donor ligands 3d series metals CFSE is small Not obey 18 e rule Tetrahedral complexes with lower CFSE t2g is non-bonding 9. On the basis of 18 VE systemClass 2: 12-18 electrons 3d metals with pi acceptor ligands (CN-)4d and 5d series metals with high OS CFSE is relatively large t2g is non-bonding Not obey 18 e rule 10. On the basis of 18 VE systemClass 3: 18 electrons Good pi acceptor ligands (CO, PF3,Arenes, olefines) CFSE is largest t2g become bonding Obey 18 e rule 11. On the basis of ligand typeClass 1: Sigma bonded ligand(A) Type of ligandsHomoleptic (MRn)Heteroleptic (MRn-aXa)(B) Hybridization on carbon atomsp3 hybridized carbonTerminalBridged 12. sp2 hybridized carbonTerminalBridged 13. sp hybridized carbonTerminalBridged 14. Class 2: Pi bonded ligandMetal-unsaturated carbon ligandEntire hydrocarbon may be involved in bondingthrough back bonding 15. Class 2: Pi bonded ligandA few of the carbon atoms of the ligand form bondwith metal 16. History of organometallic compounds 17. History of organometallic compounds 18. History of organometallic compounds 19. Nomenclature of organometallic compounds 1 Organometallic CompoundsOrganic Chemistry 6th Edition Paula Yurkanis Bruice Chapter 11 Organometallic Compounds 2 3 Organometallic CompoundsAn organic compound containing a carbonmetal bond Organolithium compounds and organomagnesium compounds are two of the most common organometallic compounds 4 Preparation of Organolithium Compounds 5 Preparation of Organomagnesium Compounds 6 7 Alkyl halides, vinyl halides, and aryl halides can all beused to form organolithium and organomagnesium compounds However, these compounds cannot be prepared from compounds containing acidic groups (OH, NH2, NHR, SH, C=CH, CO2H) 8 Coupling Reactions Preparation of the Gilman reagent:Example of carboncarbon formation using the Gilman reaction: 9 Gilman reagents can be used to prepare compoundsthat cannot be prepared by using nucleophilic substitution reactions: 10 Gilman reagents can replace halogens in compoundscontaining other functional groups: 11 The Heck Reaction 12 The Stille Reaction 13 The Suzuki Coupling 14 Mechanism of the Suzuki Coupling ReactionOxidative addition: Pd (0) to Pd (II): 15 Hydroxide exchange 16 Transmetallation: Reductive elimination: 17 Mechanism of the Heck Coupling ReactionOxidative addition: Pd (0) to Pd (II): 18 Complex formation: complex Insertion: complex 19 Undergoes oxidative addition to bromobenzeneElimination: Trans eliminationRegeneration of the catalyst: Undergoes oxidative addition to bromobenzene 1 Organometallic Chemistry 2 Organometallic CompoundsCompounds that contain a Metal-Carbon bond. Metal Alkyls, e.g. Tetraethyllead - Leaded Gas Alkyl = methyl, ethyl, tert-butyl, etc. Metal = Li, Na, K (alkali metals) Mg(alkaline earth metals) TiCrMnFe Co Ni Cu Zn Zr Ru Pd Hg OS Pt 3 Metal Alkyls General formula R-M (R = alkyl, M = metal)The C-M bond is a covalent bond! However, C--M+ or R--M+ bond tend to be polarized. This is especially true for organometallic compounds containing the more electropositive metals, i.e. alkali and alkaline earth metals. Generally, the alkyl fragment of the organometallic compound is very reactive; however this depends on the metal, changing the metal alters the polarization of the R-M bond. Thus different organometallic compounds have different reactivity. 4 Useful Metal Alkyls in Organic SynthesisC-M Bond Organomagnesium (C--Mg+) Organolithium - Li (C--Li+) Organocopper - Cu (C--Cu+) 5 Organomagnesium CompoundsGrignard Reagents Methylmagnesium chloride - CH3Mg+ Cl- Ethylmagnesium bromide - CH3CH2Mg+ Cl- Draw the structures of: Isopropylmagnesium iodide Sec-butylmagnesium chloride Formation of Grignard Reagents: CH3-Cl CH3Mg Cl Mg, Et2O 6 Reactivity of Alkyl HalidesR-I > R-Br > R-Cl Preparation of Grignards from: primary, secondary & tertiary alkyl halides. Grignard formation from aryl halides and allyl halides; however these may give Wurtz type coupling products. I2 maybe used to speed-up the formation Grignard reagents from alkyl bromides or chlorides 7 Organolithium CompoundsAlkyl Lithium Compounds Methyllithium CH3Li Ethyllithium - CH3CH2Li Draw the structures of: Isopropyllithium sec-butyllithium Alkyl lithium compounds n-propyllithium tert-butyllithium Preparation of organolithium reagents: CH3-Br CH3Li + LiBr 2 eq. Li, Et2O 8 Organocopper CompoundsLithium Dialkylcopper (organocuprate) [(R)2Cu]- Li+ Cuprates are less reactive than organolithium R acts as a Nucleophile Oxidation state of copper is Cu(I). Nucleophile R will attack various organic electrophiles. Organocuprates are used in cross-coupling reactions to form higher alkanes. Cross-Coupling Reaction: coupling of two different alkyls R and R to yield a new alkane (R-R). This type of reaction is used to make new C-C between alkyl groups. 9 Organocuprates Preparation of organocuprates:2 CH3Li [(CH3)2Cu]- Li+ + LiI As a reagent for Organic Synthesis: [(CH3)2Cu]- Li CH3CH2CH2I CH3CH2CH2CH3 Formation of new C-C bonds The electrophile CH3CH2CH2I (R-X) must be a 1 alkyl halide for a good product yield. CuI, Et2O -RCu, -LiI 10 Organic Synthesis Give a stepwise synthesis for Isobutane.2,2-dimethylpropane

Definition and classification of organometallic compounds. Classification of organometallic compounds. Classification of organometallic compounds ppt. Types of organometallic compounds. Classification of organometallic compounds with examples. Classify organometallic compounds. Names of organometallic compounds.