

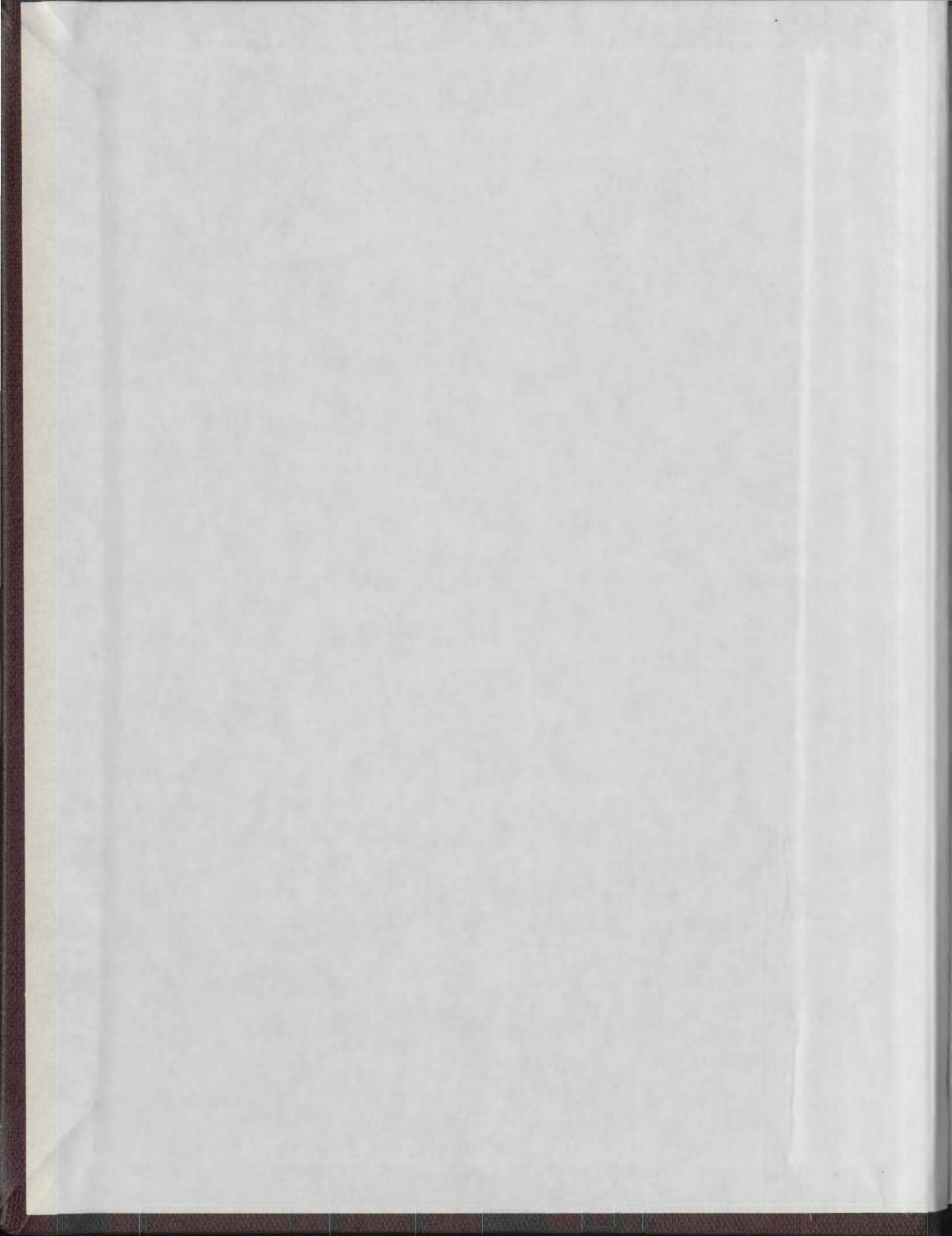
ORGANOMETALLIC COMPOUNDS
WITH METAL-METAL BONDS

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ORGANOMETALLIC COMPOUNDS WITH METAL-METAL BONDS

by



Edward Andrew Eisner, B.Sc.

A Thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

Department of Chemistry
Memorial University of Newfoundland

August 1975

St. John's

Newfoundland

SUMMARY

The compounds $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnCl}_3$, $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnBr}_3$, $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$, $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]\text{SnCl}_2$ and the novel compounds $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{SnCl}_3$, $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{SnBr}_3$, $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2\text{SnBr}_2$,* $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{SnCl}_2(\text{CO})_2\text{Fe}(\pi\text{-C}_5\text{H}_5)$,* $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{SnBr}_2(\text{CO})_2\text{Fe}(\pi\text{-C}_5\text{H}_5)$ were prepared. The nickel-containing compounds were characterised by infrared, ^1H NMR, electronic and mass spectra and samples were sent for microanalysis.

The physical parameters of the compounds are compared and the effect of varying the substituents at the tin atom on these parameters is discussed. The electron donor properties of the groups $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ and $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})$ are compared.

*These compounds have been synthesised independently by other workers in the interim between the completion of the experimental work of this thesis and its publication. See references 55 and 64 respectively.

ACKNOWLEDGEMENTS

I should sincerely like to thank Dr. M. J. Newlands for his help and encouragement throughout this work.

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My especial thanks go to my wife Monica for her support and encouragement.

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Edward A. Eisner

August 1975

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NOMENCLATURE USED IN THIS THESIS.

Common inorganic compounds are named as is customary. Compounds in which the oxidation number of an element can vary are named using Roman numerals to indicate the oxidation number of the element. (Example: tin(II) chloride - SnCl_2 .)

Organometallic compounds are named giving the radicals in this order: transition metal derived radicals (in ascending order of atomic number of the transition metal); organic radicals (aromatic before aliphatic); halogens (in ascending order of atomic number). Prefixes used are derived from the Greek - using (no prefix), bis-, tris-, for transition metal based radicals and (no prefix), di-, tri-, etc. for organic radicals or halogens. (Example: bis(carbonyl- π -cyclopentadienyl-nickel)dibromotin(IV). - $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})_2]_2\text{SnBr}_2$.)

The same convention is used when naming dimeric transition metal carbonyl derivatives. Thus, the compounds $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ and $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ are named respectively bis(dicarbonyl- π -cyclopentadienyl-iron) and bis(carbonyl- π -cyclopentadienylnickel).

INTRODUCTION

The Present State of Research in the Synthesis of Organometallic Compounds with Metal-Metal Bonds.

The number of organometallic compounds with metal-metal bonds has increased rapidly since the pioneering studies of Hein and coworkers.¹⁻⁵

In the late 1960's reviews of the work in this field were published at regular intervals^{6,7,8} -- they are now published annually under the auspices of The Chemical Society, London.^{9,10}

The compounds of interest to the present discussion are those containing a covalent bond between a transition metal (group IVa to group Ib) and a post-transition metal (group Ib to group Vb).

Table 1 shows the metal-metal bonds of this type in compounds that have been synthesised to date (July 1975). Compounds of group IVb elements predominate, probably because of the relative ease of their syntheses and their stability, or because a wide range of starting materials is available commercially in the case of compounds of group IVb elements.

Some synthetic methods are widely used and these are reviewed below, along with other syntheses of interest to this discussion.

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TABLE 1

Reports of the Synthesis of Metal-Metal Bonds Between Various Transition and Post-transition
(Earliest citation given after 1968. Reviews are used as the source up to 1972.)

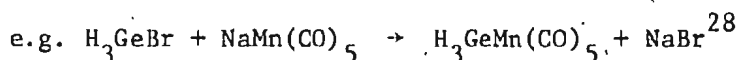
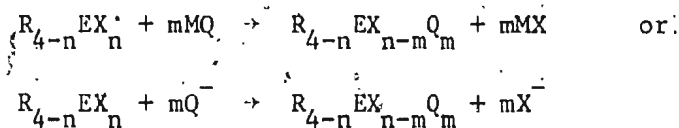
ELEMENT:	Ti	Zr	Hf	V	Nb	Ta	Cr	Mn	W	Mn	Tc	Re	Fe	Ru	Os	Co
Cu									6							11
Ag																12
Au				10	10	10	6	6	6	10			9		10	9
Zn								10		9		9	9			9
Cd										9		9	9			10
Hg						6	9	9	9	9		9	6	10		6
Al								9	9				10			10
Ga										10						6
In								9	15	9		16	9			6
Tl							17	10	18	9			18			9
Si	6	6	8	6	6	6	9	6	6	6		6	6	6	9	6
Ge	6	6	6		6	6	6	6	6	6		6	6	6	6	6
Sn	6	6	6	6		6	6	6	6	6		6	6	6	8	6
Pb	6		6	6	6		6	6	6	6		6	6		20	6
As								21	21	21			9			21
Sb							22	22	22				9			
Bi												6	9			

General Methods for the Synthesis of Metal-Metal Bonded Complexes.

1. Replacement of One or More Halogen Atom Attached to an Atom of a Post-Transition Element by a Transition Metal Carbonyl and/or Cyclopentadienyl Group.

The exchange of a halogen atom in a compound of the type $R_{4-n}EX_n$ by a transition metal group is the most widely used method for the preparation of complexes containing bonds between transition metals and post-transition metals. This type of reaction has been used to prepare complexes of group IV metals bonded to the elements chromium, molybdenum, tungsten, manganese, rhenium,⁷ iron,^{7,23-27} cobalt,⁷ nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum.²⁷ Generally, the sodium salt of the transition metal derivative is used, but the salts of other alkali metals have been used²⁷ as well as those of calcium.^{3,4}

The general equation for the reactions is as follows:



or where R = H, aryl, alkyl; E = Si, Ge, Sn, Pb; M = alkali metal or

$\frac{1}{2}Ca$; Q = $(\pi-C_5H_5)Cr(CO)_3$, $(\pi-C_5H_5)Mo(CO)_3$, $(\pi-C_5H_5)W(CO)_3$, $Mn(CO)_5$, $Re(CO)_5$,

$\frac{1}{2}Fe(CO)_4$, $(\pi-C_5H_5)Fe(CO)_2$, $Co(CO)_4$, $(\pi-C_5H_5-aR_a)Ni(CO)$, $(\pi-C_5H_5-aR_a)Ru(CO)_2$,

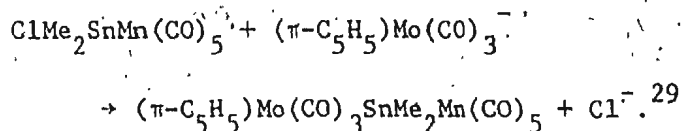
$\frac{1}{2}(\pi-C_5H_5-aR_a)Rh(CO)$, $(\pi-C_5H_5-aR_a)Pd(CO)$, $^o(\pi-C_5H_5-aR_a)Os(CO)_2$,

$\frac{1}{2}(\pi-C_5H_5-aR_a)Ir(CO)$, $(\pi-C_5H_5-aR_a)Pt(CO)$; other substituted transition

metal derivatives; X = Cl, Br, I; m, n = 1 - 4; a = 1 or 2.

Complexes can be synthesised with more than one transition metal group attached to the same atom of a group IVb element. The reaction

has been used to prepare complexes containing an atom of a group IVb element attached to atoms of two different transition metals. For example,



An analogous tungsten-tin-manganese compound was also prepared. Similarly, compounds containing Fe_2SnMo_2 skeletons,³⁰ Fe_2SnMn and Fe_2SnRe skeletons,³¹ and Fe_2SnMo skeletons^{30,32} have been made.

This preparative method appears to be limited by steric factors. Attempts to prepare tetrasubstituted derivatives of group IVb elements with manganese or rhenium pentacarbonyl have not been successful so far.^{33,34} The smaller size of the groups $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ and $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$ has enabled the existence of four such groups around a central atom of a group IVb element.^{30,31}

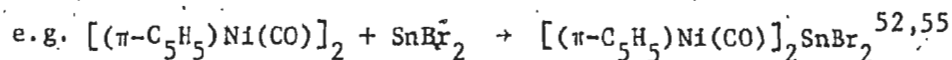
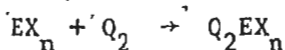
This method has been extended to complexes containing transition metal atoms bonded to atoms of group IIIb and group Vb elements. Compounds containing bonds between indium and molybdenum, tungsten, manganese, rhenium, iron,¹⁶ indium and cobalt,^{16,35} thallium and cobalt,^{18,35} thallium and manganese,³⁶ antimony and iron,^{22,37} antimony and cobalt, bismuth and iron, bismuth and cobalt,³⁷ arsenic and molybdenum, tungsten, manganese, cobalt,²¹ arsenic and iron,^{21,37} have been synthesised.

In addition, there are instances where the method has been used to form compounds containing uranium-manganese³⁸ or gold-manganese, -iron, or -cobalt³⁹ bonds.

2. Insertion of Germanium(II), Tin(II) and Indium(I) Halides into Metal-Metal, Metal-Carbon and Metal-Halogen Bonds.

Some metal-metal bonded complexes have been synthesised by insertion reactions, which are sometimes found to be convenient.

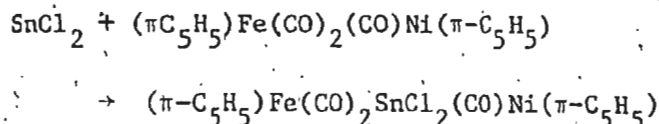
Bonds have been formed between atoms of germanium and iron,^{40,41} germanium and cobalt,⁴² germanium and ruthenium,⁴³ tin and chromium, molybdenum or tungsten,⁴⁴ tin and manganese,⁴⁵ tin and iron,^{40,42,46-49} tin and cobalt,^{42,50,51} tin and nickel,^{42,52} tin and ruthenium,⁴³ indium and chromium,⁵³ molybdenum^{15,16} or tungsten,^{15,16,53} indium and manganese,^{16,45} indium and iron,^{15,45} indium and cobalt^{45,54} by insertion into a metal-metal bond according to the reaction



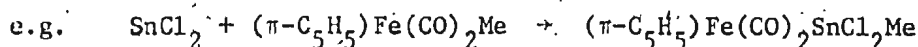
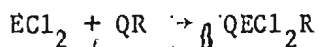
where E = Ge, Sn (n = 2) or In (n = 1); X = halogen; Q = $(\pi-C_5H_5)M(CO)_3$

(M = Cr, Mo, W), $M(CO)_5$ (M = Cr, W), $Mn(CO)_5$, $(\pi-C_5H_5)Fe(CO)_2$, $(\pi-C_5H_5)Ru(CO)_2$, $Co(CO)_4$, $(\pi-C_5H_5)Ni(CO)$ or substituted analogues of these derivatives.

Since completion of the experimental work for this thesis (August 1971), there has been a report of an insertion of tin(II) chloride into a heterobinuclear transition metal carbonyl cyclopentadienyl complex, forming a product with a heterotrimetallic skeleton.⁵⁶



Tin(II)⁵⁷ and germanium(II)^{58,59} chlorides have successfully been inserted into complexes containing an iron-carbon bond.



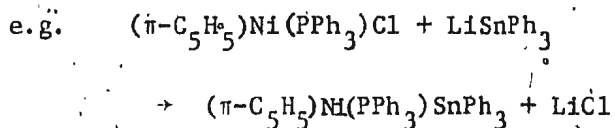
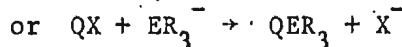
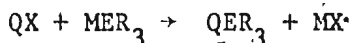
where E = Sn (R = Me, Et), Ge (R = Me, Et, n-Pr, iso-Pr, benzyl);

Q = $(\pi-C_5H_5)Fe(CO)_2$. Insertion was not observed at the tungsten-carbon bond,⁴⁶ or at the molybdenum-carbon or manganese-carbon bonds or where tin(II) bromide was used.⁵⁷ Instead, the product was a metal-metal bonded complex with three halogen atoms attached to the group IVb metal atom, i.e. of the type QEX₃.

Insertion of tin(II), germanium(II) and indium(I) halides into transition metal-halogen bonds has also been reported. Germanium(II) chloride has been inserted into iron-halogen bonds,⁶⁰ tin(II) chloride has been inserted into iron-chlorine,⁴⁶ iron-iodine,⁶¹ nickel-chlorine,^{62,63} ruthenium-chlorine,^{43,64} and palladium-chlorine⁶⁵ bonds and indium(I) halides have been inserted into molybdenum-, tungsten-, rhenium-, iron-, cobalt-, rhodium-, platinum- and gold-chlorine bonds.¹⁵

3. Reaction of Group IVb Anions with Transition Metal Carbonyl Complexes.

Some metal-metal bonds have been synthesised by the reaction of halide derivatives of transition metal carbonyl and/or cyclopentadienyl complexes with group IVb metal anions.



where Q = $(\pi-C_5H_5)ZrCl$ or $(\pi-C_5H_5)HfCl$; X = Cl; M = Li, Na; E = Si, Ge;

$R = \text{Ph};^{66}$ or $Q = (\pi\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2$; $X = \text{Br}$; $M = \text{Li}$; $E = \text{Sn}$; $R = \text{Ph};^{67}$ or

$Q = (\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$; $X = \text{Cl}$, I ; $M = (\text{Me}_3\text{NH})$; $E = \text{Ge}$; $R = \text{Cl};^{68}$ or

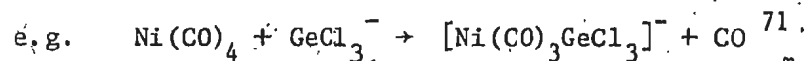
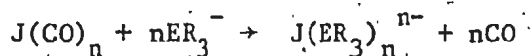
$Q = (\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{L})$ ($\text{L} = \text{triorganophosphine or -arsine or C}_6\text{H}_{11}\text{NC}$);

$X = \text{Cl}, \text{Br}$; $M = \text{Cs}$; $E = \text{Ge},^{62,69}$ $\text{Sn};^{69}$ $R = \text{Cl}, \text{Br}$; or $Q = (\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)$;

$X = \text{Cl}$; $M = \text{Li}$; $E = \text{Ge}, \text{Sn}, \text{Pb}$; $R = \text{alkyl, aryl};^{70}$ or $Q = \text{Pd}(\text{L})(\text{L}')\text{Cl}$

($\text{L}, \text{L}' = \text{alkyl or aryl isonitrile}$); $X = \text{Cl}$; $M = \text{Cs}$; $E = \text{Ge}$; $R = \text{Cl}.^{65}$

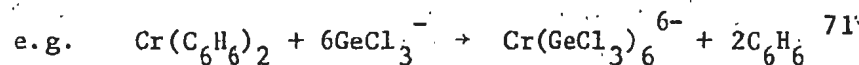
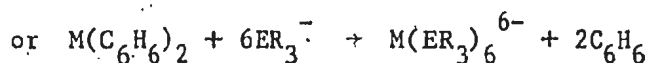
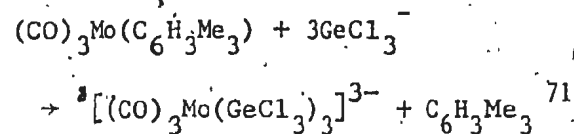
In the presence of certain group IVb anions, some transition metal carbonyl complexes lose one or more carbonyl group to form a metal-metal bond.



or where $\text{J}(\text{CO})_n = (\pi\text{-C}_5\text{H}_5)\text{V}(\text{CO})_4$, various chromium, molybdenum, tungsten or manganese carbonyl derivatives, $\text{Fe}(\text{CO})_5$, or $\text{Co}_2(\text{CO})_8$; $\text{ER}_3^- = \text{GeCl}_3^-$, SnCl_3^- , SiPh_3^- ; $n = 1, 2$.

By this type of reaction, complexes containing bonds between silicon and nickel,⁷² germanium and molybdenum,^{68,71} germanium and iron or cobalt,⁶⁸ germanium and nickel,⁷¹ germanium or tin and manganese,⁷³ tin and vanadium, chromium, molybdenum or tungsten⁷⁴ have been formed.

Group IVb anions may also displace π -bonded benzene or mesitylene in chromium or molybdenum complexes.

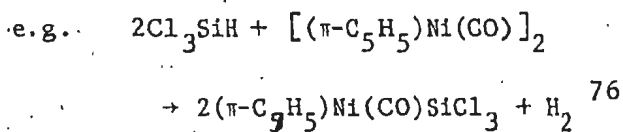
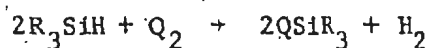


or where $M = Cr$ or Mo ; $E = Sn$.⁷⁴ Thus, complex anions with polynuclear metal-metal bonded skeletons have been prepared.

Besides the above reactions, a germanium-iron bonded complex has been prepared from the reaction of triphenylgermyllithium with the anion $HFe_3(CO)_{11}$.⁷⁵

4. Reactions of Group IVb Hydrides with Transition Metal Carbonyl Derivatives.

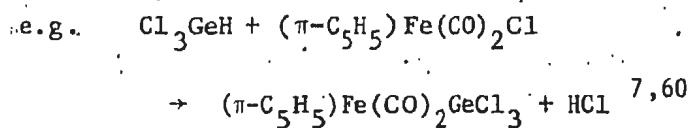
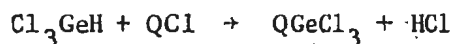
Silanes react with homobinuclear transition metal carbonyls to produce compounds with bonds between silicon and molybdenum, manganese, rhenium, iron, or nickel,⁷⁶ cobalt,⁷⁷⁻⁷⁹ and ruthenium.⁴³



or where $Q = (\pi-C_5H_5)Mo(CO)_3$, $Mn(CO)_5$, $Re(CO)_5$, $(\pi-C_5H_5)Fe(CO)_2$, $Co(CO)_4$, $(\pi-C_5H_5)Ru(CO)_2$; $R =$ alkyl, aryl, halogen.

Complexes containing silicon-iridium and germanium-iridium bonds have been synthesised by reacting an iridium carbonyl complex with trichlorosilane, trimethylsilane, or trichlorogermane.⁸⁰

Trichlorogermane has been found to react with halogen derivatives of metal carbonyls:



or where $Q = (\pi-C_5H_5)Mo(CO)_3$, $(\pi-C_5H_5)W(CO)_3$, or $Mn(CO)_5$,⁷ or

$(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{L})$ (L = trialkyl- or triarylphosphine or -arsine or $\text{C}_6\text{H}_{11}\text{NC}$).⁶²

The reaction mechanism is a matter of debate.⁷

Trialkylgermanes and stannanes have been used to prepare compounds with bonds between cobalt and germanium or tin,⁷⁷ probably in an analogous way to the reactions of the silanes.

Group IVb hydrides also react with metal carbonyls to produce metal-metal bonds. Iron-silicon⁷⁶ and iron-tin⁸¹ bonds have been prepared from iron pentacarbonyl or tri-iron dodecacarbonyl, and complexes containing ruthenium-tin bonds have been prepared from triruthenium dodecacarbonyl.⁸² Complexes containing silicon- or tin-osmium bonds have been synthesised from trimethylsilane or trimethylstannane and triosmium dodecacarbonyl.⁸³

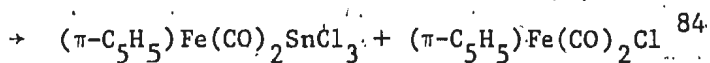
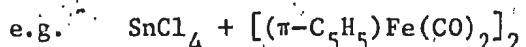
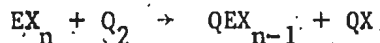
5. Reaction of Homobinuclear Transition Metal Carbonyl or Carbonyl Cyclopentadienyl Derivatives with Germanium(IV), Tin(IV), Arsenic(III), Antimony(III), Bismuth(III) Halides.

These reactions may result in the replacement of one or more halogen atom by a transition metal carbonyl or carbonyl cyclopentadienyl group, producing complexes with one or more metal-metal bond.

Before the work of this thesis, this method had not enjoyed wide application. Iron-tin,⁸⁴ cobalt-tin,^{85,86} iron-arsenic, -antimony, -bismuth,^{37,87} cobalt-bismuth³⁷ bonded complexes had been synthesised by this method.

Since then, complexes containing iron-germanium, nickel-germanium and nickel-tin bonds have also been synthesised by this method.^{52,88}

The simplest reactions of this type are thought to proceed thus:

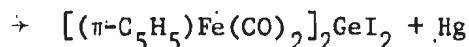
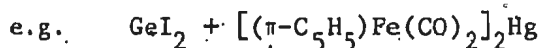


where $Q = (\pi-C_5H_5)Fe(CO)_2$, $Co(CO)_4$, $(\pi-C_5H_5)Ni(CO)$; $E = Ge, Sn$ ($n = 4$) or As, Sb, Bi ($n = 3$); $X = \text{halogen}$.

Novel trimetallic complexes have been prepared by reacting the binuclear nickel derivative with monosubstituted germanium and tin(IV) halides where the substituent is the iron group.⁸⁸ The tin derivatives were prepared as part of the work of this thesis.

6. Reactions where Mercury is Displaced from a Mercury-Transition Metal Bond by a Post-Transition Metal.

Tin(II) halides,⁸⁹ and germanium(II) iodide⁹⁰ have displaced mercury from some of its transition metal derivatives of the type $QHgR$ (where $Q = R = (\pi-C_5H_5)Mo(CO)_3$, $(\pi-C_5H_5)W(CO)_3$, $(\pi-C_5H_5)Fe(CO)_2$, for tin(II) or germanium(II) -- or where $Q = R = Co(CO)_4$, $Co(CO)_3PBu_3$ or $R = \text{halogen}$, for tin(II) halides only).

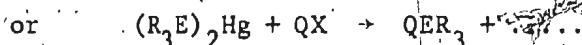
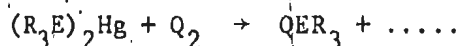


Mercury in bis(tetracarbonylcobalt)mercury has also been displaced by indium(I) halides,^{15,16} elemental zinc or cadmium,⁹¹ or elemental erbium.⁹² Indium(I) halides have also displaced mercury from bis(dicarbonyl- π -cyclopentadienyliron)mercury and bis(tricarbonyl- π -cyclopentadienylmolybdenum)mercury.¹⁵

Tin(IV) chloride has displaced mercury from various mercury iron nitrosyl carbonyl complexes, probably as mercuric chloride, producing complexes with tin-iron bonds.^{24,93} These reactions may be considered to be formally similar to the reactions described in section 1.

7. Reactions where Mercury is Displaced from a Mercury-Post-Transition Metal Bond by a Transition Metal Carbonyl and/or Cyclopentadienyl Derived Group.

Bis(triorganogermyl)mercury compounds have been treated with homobinuclear transition metal carbonyl and/or cyclopentadienyl complexes⁹⁴⁻⁹⁶ or transition metal carbonyl and/or cyclopentadienyl derived halides⁹⁵⁻⁹⁷ to produce complexes with bonds between germanium and molybdenum or tungsten,⁹⁵ iron,⁹⁴⁻⁹⁶ cobalt⁹⁶ or nickel.⁹⁵⁻⁹⁷



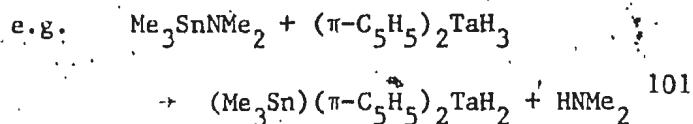
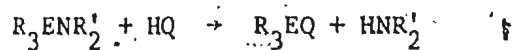
where R = phenyl,⁹⁶ ethyl;^{94,95,97} E = Ge; Q = $(\pi-C_5H_5)Mo(CO)_3$, $(\pi-C_5H_5)W(CO)_3$, $(\pi-C_5H_5)Fe(CO)_2$, $Co(CO)_4$, $(\pi-C_5H_5)Ni(PPh_3)$, $(\pi-C_5H_5)Ni(CO)$.

With the iridium complex, $Ir(PEt_3)_2(CO)Cl$, only one mercury-silicon or -germanium bond is broken in the reaction of bis(triorganosilyl)mercury or bis(triorganogermyl)mercury. Oxidative addition to the iridium atom occurs, producing both an iridium-mercury and an iridium-silicon or -germanium bond.⁸³

With iron pentacarbonyl and bis(trimethylsilyl)mercury, one carbonyl group is broken off in the formation of iron-silicon bonded complexes.⁹⁸

8. Amine Elimination Reactions.

Metal-metal bonds can be formed by the reaction

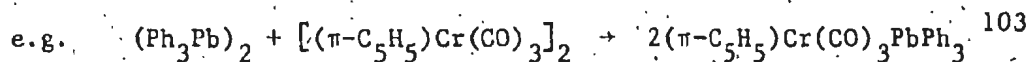
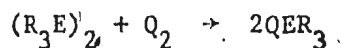


or where R, R' = alkyl, aryl; E = Ge, Sn; Q = $(\pi-C_5H_5)M(CO)_3$ (M = Cr, Mo, W),^{99,100} $(Ph_3P)_2PtCl$,¹⁰⁰ $(\pi-C_5H_5)_2MH$ (M = Mo, W),¹⁰¹ $\frac{1}{2}Os(CO)_4$.¹⁰²

This method has not enjoyed much use, possibly because the starting materials are not generally commercially available.

9. Cleavage of Homobinuclear Organo-Group IVb Compounds.

Homobinuclear organo-stannanes or -plumbanes may react with homobinuclear transition metal carbonyl cyclopentadienyl complexes with cleavage of the metal-metal bond in each compound and forming a new heterobinuclear metal-metal bond.



or where Q = $(\pi-C_5H_5)M(CO)_n$ (M = Mo, W, n = 3; M = Fe, n = 2; M = Ni, n = 1); R = CH₃; E = Sn.¹⁰⁴

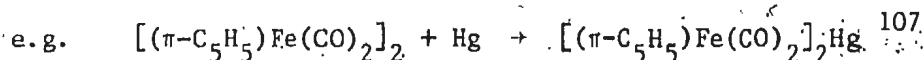
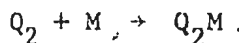
Reaction of the group IVb compounds with other transition metal carbonyl complexes also gives rise to metal-metal bonded products.

Hexaorganodistannanes have produced tin-iron, -ruthenium, -cobalt and -rhodium bonded complexes by reaction with triruthenium dodecacarbonyl,⁸² iron pentacarbonyl,⁸¹ π -cyclopentadienylcobalt dicarbonyl or π -cyclopentadienylrhodium dicarbonyl.¹⁰⁵

10. Direct Combination of Elemental Post-Transition Metals with Transition Metal Carbonyl or Carbonyl- π -cyclopentadienyl Complexes or Their Derivatives.

(In the case of mercury, this reaction can be considered formally similar to the insertion reactions discussed earlier.)

Metallic zinc, cadmium or mercury can interact with metal-metal bonds in binuclear transition metal carbonyl or carbonyl- π -cyclopentadienyl complexes to form zinc-iron or cadmium-iron,¹⁰⁶ mercury-iron,^{106,107} mercury-chromium,^{103,106,108} mercury-molybdenum or -tungsten¹⁰⁸ bonds.

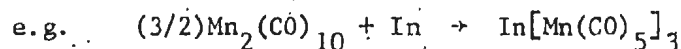
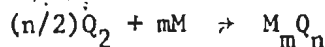


or where $Q = Fe(CO)_4^-$, $M = Zn, Cd, Hg$; $Q = Cr(CO)_5^-$, $M = Hg$; or

$Q = (\pi-C_5H_5)Z(CO)_3$ ($Z = Cr, Mo, W$), $M = Hg$.

Elements of group IIb react in a somewhat similar fashion.

Gallium-manganese or indium-manganese,¹⁰⁹ thallium-chromium or -molybdenum¹⁷ and thallium-cobalt¹¹⁰ bonds have been formed in these reactions.

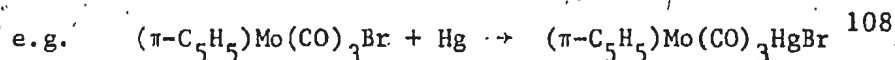
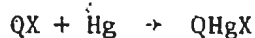


or where $Q = Mn(CO)_5$, $M = Ga$, $m = 2$, $n = 4$; $Q = (\pi-C_5H_5)Cr(CO)_3$, $M = Tl$,

$m = 1$, $n = 1, 3$; $Q = (\pi-C_5H_5)Mo(CO)_3$, $M = Tl$, $m = 1$, $n = 1$; or $Q = Co(CO)_4$,

$M = Tl$, $m = 1$, $n = 1$.

Metallic mercury has been found to react with halide derivatives of transition metal carbonyl- π -cyclopentadienyl complexes.



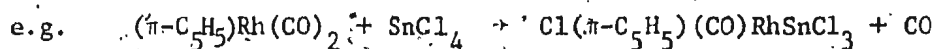
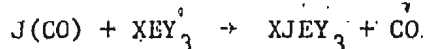
or where $Q = (\pi-C_5H_5)Mo(CO)_3$, $(\pi-C_5H_5)W(CO)_3$, $X = I$; ¹⁰⁸ or $Q = (\pi-C_5H_5)-Fe(CO)_2$, $X = Cl, I$ ¹⁰⁷.

In this way, bonds between mercury and iron, molybdenum or tungsten have been synthesised.

11. Oxidative Elimination Reactions.

Organometallic Halides of group IVb elements or tin(II), tin(IV) or germanium(IV) halides react with transition metal carbonyl moieties with loss of one carbonyl group and formation of metal-metal bonds.

Silicon-, germanium- and tin-rhodium, ¹⁹ germanium- and tin-cobalt, ¹¹¹ and tin-iron ^{112, 113} bonds have been made this way.



or where $J = (\pi-C_5H_5)Rh(CO)$, $E = Ge, Sn$, $X = Y = \text{halogen}$ or $E = Si$,

$X = H$, $Y = \text{aryl}$; or $J = (\pi-C_5H_5)Co(CO)$, $E = Ge, Sn$, $X = Y = \text{halogen}$

(except $GeCl_4$); or $J = Fe(CO)_3L$ ¹¹² ($L = PPh_3, AsPh_3, SbPh_3$), $E = Sn$,

$X = Y = Cl, Br$; or $J = Fe(CO)_4$ ¹¹³ $E = Ge, Sn$, $X = Y = \text{halogen}$.

Products of the form $J(EY_3)_2$ are found where $J = (\pi-C_5H_5)Rh(CO)$,

$XEY_3 = HSiCl_3$ or where $J = (\pi-C_5H_5)Co(CO)$, except $XEY_3 = SnI_4$.

A trimeric complex with tin-rhodium bonds ¹⁹ is formed when tin(II) chloride displaces one carbonyl group from $(\pi-C_5H_5)Rh(CO)_2$.

12. Miscellaneous Methods.

Besides those reactions already mentioned, others, much less

*where $X = Cl$, the product is Q_2Hg .

widely used, have also resulted in the formation of metal-metal bonds.

It is beyond the scope of this discussion to consider them all in detail.

However, those of especial interest here will be outlined below.

Some complexes containing bonds between tin and molybdenum, manganese, iron, cobalt, nickel have been synthesised using tris-(trimethylstannyl)amine or bis(trimethylstannyl)oxide and the appropriate homobinuclear transition metal carbonyl derivative.¹¹⁴ It was not possible to account for the fate of the nitrogen or the oxygen. For example, the compound $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{SnMe}_3$ was prepared from $(\text{Me}_3\text{Sn})_3\text{N}$ and $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$.

A complex containing indium-cobalt bonds has been prepared from trimethylindium and tetracarbonylcobalt hydride with elimination of methane.¹⁶

Thallium^{110,115} and magnesium¹¹ derivatives of transition metal carbonyl complexes have been used to synthesise other compounds containing new metal-metal bonds. The reactions of these substances are in some ways analogous to the reactions described in section 1 and the last ones of section 6 or those of section 7.

Assorted addition reactions have produced complexes with iridium-silicon and -germanium,¹¹⁶ iridium-gold, -copper and rhodium-copper¹¹⁷ and nickel-tin¹¹⁸ bonds.

By various other reactions, complexes containing bonds between tin and the metals chromium,^{119,120} molybdenum and tungsten,¹²⁰ iron,¹²¹ ruthenium^{122,123} are reported to have been prepared.

Complexes Containing Bonds between Nickel and a Group IVb Element.

Complexes containing a metal-metal bond between nickel and a post-transition element have received less attention than those of other transition metals. The only ones known are those where the post-transition metal is a member of group IVb.

The earliest report of complexes with bonds between nickel and group IVb elements is dated 1961,²⁷ where these were prepared using the anion $(\pi-C_5H_5)Ni(CO)^-$ or similar anions where the cyclopentadienyl ring has organic substituents.

Since then, these complexes have been synthesised by most of the other methods described earlier, with the exception of those in section 6 -- since no complex with a mercury-nickel bond has yet been reported.

The experimental work of this thesis was done with a view towards applying some of the commonly used synthetic methods to the preparation of complexes containing a nickel-tin bond. An area of especial concentration was the reaction of tin(IV) halides or substituted halides with bis(carbonyl- π -cyclopentadienylnickel), which, where successful, yielded some novel compounds with relative ease. Insertion reactions were also studied.

EXPERIMENTAL WORK

Starting materials were generally obtained commercially. Of those that were not, the preparations are described below. The compounds, bis(dicarbonyl- π -cyclopentadienyliron) and bis(carbonyl- π -cyclopentadienyl-nickel) were obtained from Alfa Inorganics Inc., Beverly, Massachusetts, U.S.A.

Preparations were carried out under an atmosphere of dry nitrogen. Solvents were kept over sodium -- diethyl ether and tetrahydrofuran were kept over sodium benzophenone ketyl -- and all were distilled under vacuum before use.

Infrared spectra were run as Nujol or hexachlorobutadiene mulls between sodium chloride plates on a Perkin-Elmer model 457 infrared spectrophotometer, or as chloroform solutions in 0.5mm KBr cells on a Perkin-Elmer model 225 infrared spectrophotometer. Calibration standards of DCl and polystyrene were employed in the range 2200-1900 cm^{-1} .

Ultraviolet spectra were run as CHCl_3 solutions in quartz cells on a Unicam SP800 spectrophotometer.

NMR spectra were recorded on a Varian A60 instrument. CDCl_3 was used as the solvent for these spectra, and tetramethylsilane was used as a reference.

Mass spectra were obtained using a Perkin-Elmer-Hitachi RMU-6E instrument with the direct insertion probe.

Elemental analyses were carried out by the Alfred Bernhardt Microanalytical Laboratories, West Germany.

Preparation of tin(IV) iodide.

Powdered tin (2.4g, 20mmole) and solid iodine (10.1g, 40mmole) were mixed in carbon tetrachloride (50ml). The mixture was refluxed until no further colour change (from purple to orange-red) was noted. Solvent was removed and the residue was extracted with carbon tetrachloride, filtered and cooled. Crystals of tin(IV) iodide (10.4g, 17mmole, 85%) were obtained, m.p. $142-3^{\circ}$ (lit. 143.5° ¹²⁴).

Preparation of tin(IV) bromide.

Small pieces of metallic tin (2.4g, 20mmole) were placed in a three-necked flask, through which dry nitrogen gas was continuously passed. A reflux condenser was fitted to the middle neck. Bromine (7.0g, 44mmole) was added dropwise down the reflux condenser. Vigorous reaction was observed, during which a colourless liquid, tin(IV) bromide, formed. Excess bromine was distilled off, and then the remaining liquid was distilled into another container. The product was purified by cooling it until most of it solidified, and the remaining liquid was decanted. The solid was remelted and cooled to solidify most of it and again the excess liquid was decanted to leave purified tin(IV) bromide (4.8g, 11mmole, 55%), m.p. $32-3^{\circ}$ (lit. 33° ¹²⁴).

Preparation of (dicarbonyl- π -cyclopentadienyliron)trichlorotin(IV).

Tin(IV) chloride (9.7ml, 22g, 85mmole) was added to dry, oxygen-free benzene (500ml) in a 1000ml round-bottomed flask fitted with a reflux condenser and a Soxhlet extractor. Bis(dicarbonyl- π -cyclopentadienyliron) (30g, 85mmole) was placed in the thimble inside the extractor. The solution was refluxed until all the solid in the thimble was extracted. The solution was filtered and its volume was reduced by

evaporation under vacuum until a solid began to separate out. Recrystallisation in dichloromethane yielded orange crystals of (dicarbonyl- π -cyclopentadienyliron)trichlorotin(IV) (21g, 51mmole, 60%), m.p. 156-7°; dec. (lit. 150°, ^{27,125} 155-7°, ¹²⁶ 157°^{46,84}).

Preparation of (dicarbonyl- π -cyclopentadienyliron)-tribromotin(IV).

Similar method to that used above, using tin(IV) bromide (6.6g, 15mmole), bis(dicarbonyl- π -cyclopentadienyliron) (5.3g, 15mmole) in benzene (150ml), yielded (dicarbonyl- π -cyclopentadienyliron)tribromotin(IV) (2.4g, 4.6mmole, 30%), m.p. 170° (lit. 169-170°, ¹²⁶ 170-1°⁸⁴).

Reaction of bis(dicarbonyl- π -cyclopentadienyliron) with tin(II) chloride dihydrate.

Tin(II) chloride dihydrate (4.1g, 18mmole) and bis(dicarbonyl- π -cyclopentadienyliron) (5.3g, 15mmole) were mixed in methanol(250ml) and ethyl acetate(50ml) and the solution was refluxed in an atmosphere of dry nitrogen for 6 hours. The colour of the solution had changed from wine-red to orange in this time. On cooling, orange crystals of bis(dicarbonyl- π -cyclopentadienyliron)dichlorotin(IV) separated from the solution. Removal of some solvent under vacuum left 50ml of concentrated solution which, on cooling, yielded a further quantity of the same material.

The orange crystals were washed with hexane and recrystallised from methanol to give fine orange needles of bis(dicarbonyl- π -cyclopentadienyliron)dichlorotin(IV) (5.4g, 10mmole, 67%), m.p. 167-8° (lit. 166-8°, ^{46,89} 167-8°, ¹²⁶ 168°^{31,84}).

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with anhydrous tin(II) chloride.

Anhydrous tin(II) chloride (0.64g, 3.4mmole) and bis(carbonyl- π -cyclopentadienylnickel) (1.0g, 3.3mmole) were mixed and dry oxygen-free tetrahydrofuran was condensed onto the solids to dissolve them. The solution was stirred under reflux until there was no evidence of bridging carbonyl bands ($1800-1900\text{cm}^{-1}$) in the infrared spectra of the solution (2 hours). Solvent was removed under vacuum, and the remaining solid was extracted with chloroform. The product was recrystallised from 1:1 CHCl_3 /hexane, giving dark green plates of bis(carbonyl- π -cyclopentadienylnickel)dichlorotin(IV) (0.68g, 1.4mmole, 42%), m.p. $93-94^\circ$ (lit. 90° (dec.)⁴²).

Analysis: Calc'd: C, 29.22%; H, 2.04%; Cl, 14.38%.

Found : C, 29.27%; H, 2.12%; Cl, 14.54%.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with anhydrous tin(II) bromide.

Dry tetrahydrofuran (50ml) was condensed into a 100ml round-bottomed flask containing bis(carbonyl- π -cyclopentadienylnickel) (1.0g, 3.3mmole) and tin(II) bromide (1.0g, 3.5mmole). The solution was stirred under reflux until there was no trace of bridging carbonyl bands ($1800-1900\text{cm}^{-1}$) in infrared spectra of samples of the mixture (2 hours). Solvent was removed under vacuum and the solid was extracted with chloroform, which, on cooling to -63° and removal of some solvent under vacuum, gave a dark green crystalline solid.

The solid was recrystallised from 1:1 CHCl_3 /hexane to give dark green plates of bis(carbonyl- π -cyclopentadienylnickel)dibromotin(IV)

(0.66g, 1.1mmole, 34%), m.p. 107-108°.

Analysis: Required: C, 24.76%; H, 1.73%; O, 5.50%; Br, 27.45%.

Found : C, 24.76%; H, 1.88%; O, 5.66%; Br, 27.37%.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with tin(II) iodide.

Tin(II) iodide (1.3g, 3.5mmole) and bis(carbonyl- π -cyclopentadienylnickel) (1.0g, 3.3mmole) were dissolved in dry, oxygen-free tetrahydrofuran (50ml). The mixture was stirred for two hours, after which a change of colour, from cherry-red to dark brown was noted. Removal of the solvent left a tarry residue. This was extracted into benzene, and removal of the solvent left another tarry residue, apparently unchanged.

The process was repeated, this time extracting the residue into dichloromethane, with the same result. It proved impossible to obtain a pure product.

Infrared spectra of the tarry residue showed a very strong band at 2070cm^{-1} .

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with tin(IV) chloride.

Tin(IV) chloride (0.4ml, 0.90g, 3.5mmole) and bis(carbonyl- π -cyclopentadienylnickel) (1.0g, 3.3mmole) were mixed in dry, oxygen-free benzene (30ml) and stirred at room temperature under nitrogen for 40 minutes. The resulting green solution was filtered, benzene was removed under vacuum until the volume of the solution was reduced to 10ml and an equal volume of hexane was added dropwise. Dark green needles were obtained which were recrystallised by dissolving in benzene (10ml) and depositing with hexane added dropwise. The product was filtered and dried to give (carbonyl- π -cyclopentadienylnickel)trichlorotin(IV) (0.46g,

1.2mmole, 37%), m.p. 42-43°(dec.).

Analysis: Required: C, 19.12%; H, 1.34%; Cl, 28.22%.

Found : C, 18.91%; H, 1.43%; Cl, 28.34%.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with tin(IV) bromide.

Tin(IV) bromide (1.7g, 4.0mmole) and bis(carbonyl- π -cyclopentadienylnickel) (1.0g, 3.3mmole) were mixed in dry, oxygen-free benzene (40ml) and stirred at room temperature under nitrogen for one hour. The resulting green solution was filtered and concentrated to 5ml by removing benzene under vacuum. Hexane (20ml) was added dropwise until fine, dark green needles were obtained. The product was recrystallised by dissolving in benzene and adding hexane dropwise to the solution, which was then filtered and the solid was dried to give crystals of (carbonyl- π -cyclopentadienylnickel)tribromotin(IV) (0.52g, 1.2mmole, 36%), m.p. 56-58°(dec.).

Analysis: Required: C, 14.12%; H, 0.99%; Br, 46.98%.

Found : C, 13.97%; H, 1.06%; Br, 47.08%.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with tin(IV) iodide.

Tin(IV) iodide (2.0g, 3.2mmole) and bis(carbonyl- π -cyclopentadienylnickel) (0.91g, 3.0mmole) were mixed in dry, oxygen-free benzene (50ml). The solution was stirred at room temperature for two hours, during which the solution had changed colour from wine-red to brown. Removal of solvent under vacuum left a brown tarry residue. The residue was extracted into benzene and filtered. The benzene was removed under vacuum, and a similar tarry residue was left. Extraction with other solvents gave no pure product. The material decomposed before it could be purified. (According to infrared spectra, no absorptions could be

seen in the carbonyl stretching region -- $1700-2100\text{cm}^{-1}$.)

Infrared spectra of the tarry residues showed a very strong band at about 2070cm^{-1} .

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with (dicarbonyl- π -cyclopentadienyliron)trichlorotin(IV).

(Dicarbonyl- π -cyclopentadienyliron)trichlorotin(IV) (1.5g, 3.7mmole) and bis(carbonyl- π -cyclopentadienylnickel) (1.2g, 3.9mmole) were mixed together in dry, oxygen-free benzene (50ml) and the mixture was refluxed under nitrogen for 12 hours. During this time, the progress of the reaction was monitored by infrared spectroscopy, watching for the disappearance of the bridging carbonyl bands in the $1800-1900\text{cm}^{-1}$ range. The solvent was removed under vacuum, leaving a dark brown solid. The solid was washed with hexane and extracted into a 1:1 mixture of dichloromethane/hexane and filtered under nitrogen. Concentration of the solution with cooling yielded brown-green crystals which were washed, filtered and dried under a stream of dry nitrogen. Recrystallisation with the same solvent mixture gave (dicarbonyl- π -cyclopentadienyliron)-(carbonyl- π -cyclopentadienylnickel) dichlorotin(IV) (1.0g, 1.9mmole, 52%), m.p. $113-114^\circ$.

Analysis: Required: C, 30.12%; H, 1.94%; Cl, 13.68%.

Found : C, 30.20%; H, 2.08%; Cl, 13.48%.

It was noted that under vacuum, a green volatile solid, which proved to be nickelocene, was given off in observable quantities in this preparation.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with (dicarbonyl- π -cyclopentadienyliron)tribromotin(IV).

(Dicarbonyl- π -cyclopentadienyliron)tribromotin(IV) (2.0g, 2.6mmole) and bis(carbonyl- π -cyclopentadienylnickel) (0.85g, 2.8mmole) were mixed together in dry, oxygen-free benzene (50ml) and the mixture was refluxed under nitrogen for 12 hours until there was no carbonyl bridging band in the range 1800-1900 cm^{-1} in infrared spectra of the mixture. The solvent was removed under vacuum, leaving a dark brown solid. This was washed with hexane to remove traces of unreacted bis(carbonyl- π -cyclopentadienylnickel) and then extracted into a 1:1 mixture of dichloromethane/hexane and filtered under nitrogen. The solution was concentrated and cooled, giving brown-green crystals. These were washed with hexane, filtered, and dried under a stream of dry nitrogen. Recrystallisation with the same solvent mixture gave (dicarbonyl- π -cyclopentadienyliron)(carbonyl- π -cyclopentadienylnickel)dibromotin(IV) (1.0g, 1.7mmole, 65%), m.p. 148-149°.

It was noted that nickelocene was given off in observable amounts in this preparation, especially where there was a vacuum.

Analysis: Required: C, 25.71%; H, 1.66%; Br, 26.32%.

Found : C, 25.54%; H, 1.80%; Br, 26.34%.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with tin(II) fluoride.

This was done under similar reaction conditions to reactions with other tin(II) halides. Infrared spectroscopy of the reaction mixture at regular intervals showed bridging carbonyl bands in the region 1800-1900 cm^{-1} , indicating that the intended reaction had not taken place (insertion).

The reaction mixture was refluxed for longer periods, eventually yielding

materials that gave no evidence of having carbonyl bands at all in their infrared spectra. No crystalline products were obtained.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with potassium metal.^{27,127}

Several attempts were made to prepare the anion, $[(\pi-C_5H_5)Ni(CO)]^-$, by the reaction of these two materials using equimolar quantities in tetrahydrofuran solutions. At room temperature, there was no apparent reaction. No colour change was observed and infrared spectra of the solutions at regular intervals showed no change in the bridging carbonyl region at $1800-1900\text{cm}^{-1}$. At elevated temperatures, the solution changed from wine-red to green and infrared spectra of the resulting mixture showed a band at about $1740-1745\text{cm}^{-1}$, characteristic of the compound $[(\pi-C_5H_5)Ni]_3(CO)_2$.¹²⁸

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with sodium metal.

These materials were taken in equimolar quantities in tetrahydrofuran solution under the same conditions as the reaction with potassium metal. At room temperature, the solution went green, and infrared spectra of the resulting mixture showed a band at about $1740-1745\text{cm}^{-1}$ as before.¹²⁸

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with phenyltin trichloride.

This reaction was done under the same conditions as for reactions with tin(IV) halides. The reaction mixture after one hour gave infrared spectra with a strong sharp band at about 2020cm^{-1} . Removal of solvent gave a greenish-brown oil from which it was not possible to obtain a

pure product before decomposition set in.

Reaction of bis(carbonyl- π -cyclopentadienylnickel) with diphenyltin dichloride.

This reaction was done using equimolar quantities of the reactants. The materials were refluxed in benzene for 19 hours. The crude product gave a band at about $2000\text{--}2005\text{cm}^{-1}$. This also was impossible to purify.

Reaction of bis(carbonyl- π -cyclopentadienylnickel)dibromo tin(IV) with phenyllithium.

These materials were taken in a molar ratio of 1:2 and added together in tetrahydrofuran at -78° . The mixture was stirred at that temperature for 20 hours. Infrared spectra of the resulting mixture showed only a weak, broad band at about 1950cm^{-1} . Removal of solvent under vacuum left an oil from which it was not possible to obtain a pure crystalline product.

Reaction of bis(carbonyl- π -cyclopentadienylnickel)dibromo tin(IV) with methylmagnesium iodide.

These materials were taken in a molar ratio of 1:2 and added together in diethyl ether at room temperature. The mixture was stirred for 24 hours. An infrared spectrum of the mixture immediately after the reactants were added together showed bands in the bridging carbonyl region, $1800\text{--}1900\text{cm}^{-1}$, as well as one at 1750cm^{-1} , and one at 2060cm^{-1} . After 24 hours, an infrared spectrum showed a band at 2000cm^{-1} together with the bridging carbonyl bands. Attempts to isolate a pure product were unsuccessful.

Reaction of bis(carbonyl- π -cyclopentadienylnickel)dichlorotin(IV) with thiophenol in presence of a base.

The reactants were taken in the molar ratio 1:1.1 with a slight excess of triethylamine in tetrahydrofuran at room temperature. After one hour, an infrared spectrum of the mixture showed a band at about 1995cm^{-1} together with one at about 1950cm^{-1} and at about 1810cm^{-1} . After a further hour, solvent was removed under vacuum, leaving an oil. Infrared spectra of this oil showed a band at about 1995cm^{-1} . Attempts to purify the material were unsuccessful.

Reaction of bis(carbonyl- π -cyclopentadienylnickel)dichlorotin(IV) with ethanethiol in presence of a base.

This was done in the same manner as above, with equally negative results. No consistent spectra were recorded.

DISCUSSION

I. The Reactions.

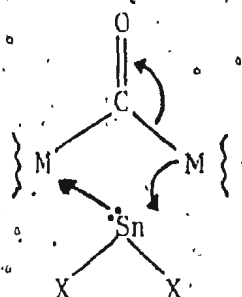
The insertion of tin(II) chloride or bromide into the nickel-nickel bond of $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ takes place quite readily when tetrahydrofuran is used as a solvent, the products being $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2\text{SnX}_2$ ($\text{X} = \text{Cl}$ or Br respectively). The insertion of tin(II) chloride takes place readily into $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ with methanol as the solvent, as previously reported.⁴⁶

Insertion of tin(II) halides into binuclear transition metal carbonyl complexes has been reported by some researchers to take place most readily when the transition metal complex contains bridging carbonyl groups.^{42,46} There are reports, however, of insertion into chromium-chromium, molybdenum-molybdenum, tungsten-tungsten,⁴⁴ manganese-manganese,⁴⁵ and cobalt-cobalt^{50,51,129} bonded complexes where the metal-metal bond is unsupported by bridging carbonyl groups. It is reported that, in the case of the cobalt-cobalt⁴² and manganese-manganese⁴⁵ bonds, conditions must be more rigorous in order to effect insertion where there is no bridging carbonyl group present in the original transition metal complex.

Infrared spectra of solutions of the complexes $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ¹³⁰ and $\text{Co}_2(\text{CO})_8$ ¹³¹⁻¹³⁵ show mixtures of bridged and unbridged forms in varying proportions, depending on the temperature. It may be that insertion intermediates requiring lower activation energies are possible where bridged-nonbridged isomerism occurs.

A steric factor may also be responsible for the differences in reactivity of the binuclear transition metal complexes. Because of the larger number of carbonyl groups around the transition metal atoms, $Mn_2(CO)_{10}$ would be expected to be less reactive than $Co_2(CO)_8$ and $[(\pi-C_5H_5)M(CO)_3]_2$ ($M = Cr, Mo, W$) would be expected to be less reactive than $[(\pi-C_5H_5)Fe(CO)_2]_2$ and even less reactive than $[(\pi-C_5H_5)Ni(CO)]_2$ where insertion of a tin(II) halide is concerned.

Kinetic studies of the insertion of tin(II) halides into the metal-metal bond of the binuclear complexes $[(\pi-C_5H_5)Fe(CO)_2]_2$,¹³⁶ $[(Bu_3P)Co(CO)_3]_2$,¹³⁷ $[(\pi-C_5H_5)Ni(CO)]_2$ ⁵⁵ have been reported. The results suggest a bimolecular mechanism in which the dimer is subjected to a direct attack by the tin(II) halide species. A postulated intermediate is shown below ($M = Fe, Co$).



In the case of insertion of tin(II) halides into nonbridged dimeric species, for example, $[(\pi-C_5H_5)Mo(CO)_3]_2$,⁴⁴ or $[(Bu_3P)Co(CO)_3]_2$,¹²⁹ it is suggested that there are two possible mechanisms -- direct and indirect. In the latter, there is first formed a mixture of QX and $QSnX_3$, after which the excess dimer reacts with the $QSnX_3$ to form Q_2SnX_2 ($Q = (\pi-C_5H_5)Mo(CO)_3, (Bu_3P)Co(CO)_3$, or other similar transition metal derived group; $X =$ halogen). The presence of QX, $QSnX_3$, Q_2SnX_2 among the

reaction mixtures is taken as evidence in support of the suggested reaction scheme. The relative importance of the two pathways depends on the nature of the transition metal group, the halogen, the solvent used, the mole ratio of the reactants, the temperature, and the presence or absence of light.

In the light of some of these considerations, the ease of reaction of tin(II) chloride and bromide with the nickel dimer seems reasonable.

Apparently, tin(II) fluoride does not insert into the nickel-nickel bond when tetrahydrofuran is used as the solvent, as infrared spectra of the reaction mixtures taken at intervals show bridging carbonyl groups to be present at all times. However, the lack of reaction may be due to the two species not being in the same phase, as tin(II) fluoride is practically insoluble in tetrahydrofuran, or indeed most solvents.

Tin(II) iodide gives a brown tarry product when reacted with the nickel dimer. This product is volatile, having an extremely disagreeable odour. It decomposes too rapidly for it to be isolated, and no other materials could be isolated for identification. The product may be the unstable compound $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{I}$.¹³⁸

Tin(IV) chloride and bromide react readily with $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ in benzene to give $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{SnX}_3$ (X = Cl or Br respectively). In neither case was it possible to isolate the other expected product, carbonyl- π -cyclopentadienyl halide, presumably because of decomposition due to thermal instability.

Carbonyl- π -cyclopentadienylnickel iodide has been identified and found to be unstable above 0°. ¹³⁸ Among other transition metal carbonyl

halides, the stabilities tend to fall in the order $\text{Cl} < \text{Br} < \text{I}$ with very few fluoro- derivatives known.¹³⁹ Assuming that, as with other metal carbonyl halides, the iodide is the least electron-attracting, with the bromide more so, and the chloride most attracting, the electron density at the metal atom would be expected to be least in the chloride. Thus, the extent of backbonding from the metal $d\pi$ to the carbon $p\pi$ orbitals would be reduced, weakening the metal-carbon bond, making decomposition easier.

For example, of the compounds $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$; the chloride decomposes at 87° ¹⁴⁰ without melting, whereas the iodide only decomposes at $117\text{--}118^\circ$ as it melts.¹⁴¹ Also, experiments on the rate of CO exchange in the compounds $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ show that the rate is greatest when $\text{X} = \text{Cl}$, less when $\text{X} = \text{Br}$, and least when $\text{X} = \text{I}$ ¹⁴² -- evidence for the difference in bond strengths between the metal and the carbon atoms and also suggestive of the ease with which a CO group may leave a chloride derivative compared to the corresponding iodide derivative. The authors also studied the exchange rate in the compounds $\text{Mn}(\text{CO})_5\text{X}$ with similar results. Observations of the stabilities of the compounds $\text{Co}(\text{CO})_4\text{X}$ show that they decrease in the order $\text{X} = \text{I} > \text{Br} > \text{Cl}$.¹⁴³

Reaction of tin(IV) iodide with the binuclear nickel complex apparently gives products similar to those when tin(II) iodide is used.

Although organotin(IV) halides appear to react with the binuclear nickel complex in a similar fashion to the reaction of tin(IV) halides, producing similar colour changes and changes in the infrared spectra of the mixtures, no products could be isolated to confirm this.

The compounds $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnX}_3$ ($\text{X} = \text{Cl}, \text{Br}$) react with the nickel complex in much the same way as tin(IV) chloride and bromide, the

products being novel heterotrimetallic compounds containing a tin atom bonded to an iron atom and a nickel atom, $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnX}_2(\pi\text{-C}_5\text{H}_5)\text{-Ni}(\text{CO})$ ($\text{X} = \text{Cl}, \text{Br}$).

Attempts to prepare the anion, $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})^-$, were not successful. It had been hoped that some novel metal-metal bonded complexes could have been made using the anion to displace halogen atoms attached to tin atoms in tin(IV) compounds.

Attempts to produce novel compounds by replacement of the halogen atoms in $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2\text{SnX}_2$ by other groups were likewise unsuccessful. In the reaction of methylmagnesium iodide with $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2\text{SnBr}_2$, it appeared that the tin-nickel bond was broken, with the formation of $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2$ and $[(\pi\text{-C}_5\text{H}_5)\text{Ni}]_3(\text{CO})_2$. (Infrared spectra of the reaction mixture showed absorptions at about $1740\text{-}1745\text{cm}^{-1}$ and in the range $1800\text{-}1900\text{cm}^{-1}$, characteristic of these compounds.)

2. Physical Properties of the Products.

The products that were successfully isolated from reactions were all crystalline materials. The nickel-tin complexes were green, the nickel-tin-iron complexes were brown-green and the iron-tin complexes were orange in colour.

The stability of the products varied considerably. The monosubstituted nickel-tin complexes decomposed rapidly on exposure to the atmosphere both as solids and in solution. They decomposed slowly even as solids under dry nitrogen in absence of light, the product of decomposition being a black or grey-black powdery solid. The disubstituted nickel-tin complexes in the solid state were relatively stable on exposure to air, but solutions decomposed slowly. The compounds containing the

iron group were stable as solids and decomposed only very slowly as solutions when exposed to the atmosphere. Interestingly, the mixed metal compounds gave off some nickelocene when subjected to low pressures.

The metal-metal bonded complexes were soluble in most organic solvents, although less so in saturated hydrocarbons. This property was made use of in isolating and purifying them.

Table 2 summarises some of the physical and spectroscopic properties of the nickel complexes synthesised here.

3. Suggested Structures for the Products.

At present, the only cyclopentadienylnickel compound containing a nickel-metal bond for which a crystal structure has been determined is $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)\text{GeCl}_3 \cdot \frac{1}{2}\text{C}_6\text{H}_6$.⁶⁹

In this compound, the cyclopentadienyl ring is distorted. The nickel, germanium and phosphorus atoms lie in a plane perpendicular to the mean plane of the cyclopentadienyl ring. One of the chlorine atoms lies almost in plane with the nickel, germanium and phosphorus atoms. A diagram of the molecule is shown in Figure 1, following Table 2. The bond lengths and angles are not to scale.

In the absence of other x-ray structural determinations, it is assumed that the geometry around the nickel atom in the carbonyl- π -cyclopentadienylnickel compounds reported in this thesis is similar, following a distorted trigonal bipyramidal configuration around the nickel atom, in which two equatorial and one axial position are occupied by the cyclopentadienyl ring, as shown in Figure 2. In this way, the centre of the ring and the nickel, the group IVb metal atom and the ligand can all lie in one plane.

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TABLE 2

Physical Parameters of the Nickel Compounds Prepared.

Compound	Colour	m. p.	ν_{C-O} (cm^{-1})	$\tau_{C_5H_5}^c$
$[(\pi-C_5H_5)Ni(CO)]_2SnCl_2$	green	93-94°	2088w, 2045s, 2028s ^d	4.42
$[(\pi-C_5H_5)Ni(CO)]_2SnBr_2$	green	107-8°	2030s, 2019mw ^a	4.43
$(\pi-C_5H_5)Ni(CO)SnCl_3$	green	42-43° dec	2071s, 2021w* ^a 2072s ^d	4.18
$(\pi-C_5H_5)Ni(CO)SnBr_3$	green	56° dec	2065s, 2016w* ^a 2069s ^d	4.23
$(\pi-C_5H_5)Ni(CO)SnCl_2-$ $(CO)_2Fe(\pi-C_5H_5)$	brown- green	113-4°	2028s, 2007ms, 1994ms, 1960ms ^a 2034s, 2008s, 1968s ^b	4.43 4.92
$(\pi-C_5H_5)Ni(CO)SnBr_2-$ $(CO)_2Fe(\pi-C_5H_5)$	brown- green	148-9°	2031ms, 2003s, 1964s ^a 2035s, 2006s, 1968ms ^b	4.45 4.96

^a As Nujol mull between NaCl plates.^b As $CHCl_3$ solution in 0.5mm KBr cell.^c As $CDCl_3$ solution; TMS reference^d As $CHCl_3$ solution in 0.1mm NaCl cell.

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prepared.

m. p.	ν_{C-O} (cm ⁻¹)	$\tau_{C_5H_5}^c$	λ_{max} (nm)	Ions in mass spectrum
-94°	2088w, 2045s, 2028s ^d	4.42	238sh, 261ms, 296m	P-CO, P-2CO, P-SnCl ₂ , (C ₅ H ₅) ₂ Ni ₂ CO, (C ₅ H ₅) ₂ Ni ₂ , SnCl ₂ , (C ₅ H ₅)Ni, SnCl, etc.
-7-8°	2030s, 2019mw ^a	4.43	244s, 275vs, 308sh, 444w	P-CO, P-2CO, P-SnBr ₂ , (C ₅ H ₅) ₂ Ni ₂ CO, (C ₅ H ₅) ₂ Ni ₂ , (C ₅ H ₅) ₂ Ni, SnBr ₂ , (C ₅ H ₅)Ni, SnBr, etc.
-43°dec	2071s, 2021w* ^a 2072s ^d	4.18	>250, 302m, 446m	P, P-CO, (C ₅ H ₅) ₂ Ni, SnCl ₂ , (C ₅ H ₅)NiCl, (C ₅ H ₅)Ni
°dec	2065s, 2016w* ^a 2069s ^d	4.23	235m, 280m, 361mw	(C ₅ H ₅) ₂ Ni, (C ₅ H ₅)Ni ^e
-3-4°	2028s, 2007ms, 1994ms, 1960ms ^a 2034s, 2008s, 1968s ^b	4.43 4.92	240s, 288ms	P, P-CO, P-2CO, P-3CO
-8-9°	2031ms, 2003s, 1964s ^a 2035s, 2006s, 1968ms ^b	4.45 4.96	242m, 270vs, 306sh, 412w	P, P-CO, P-2CO

^cAs CCl₄ solution; TMS reference^eNo better mass spectrum available^dAs CHCl₃ solution in 0.1mm NaCl cell*Attributed to ¹³C-O stretch.

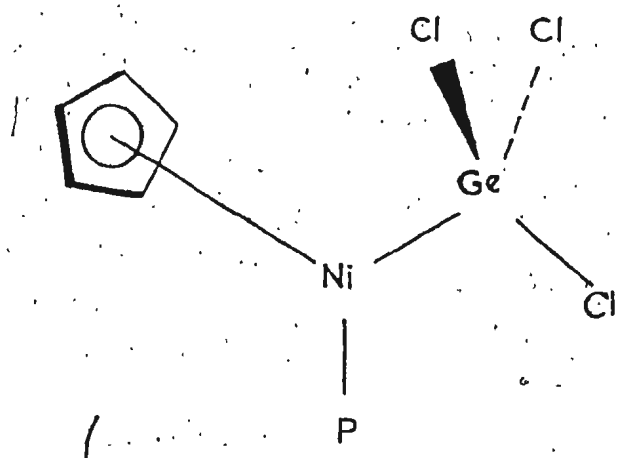


Fig. 1

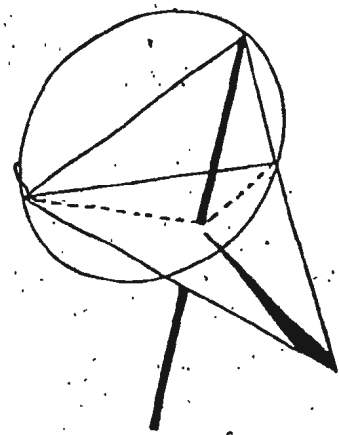


Fig 2a

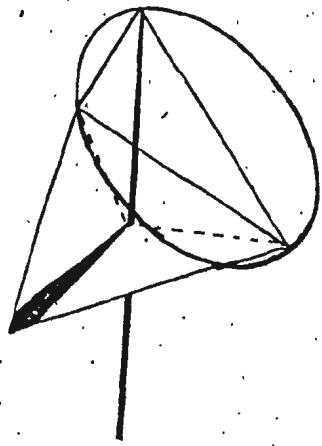


Fig 2b

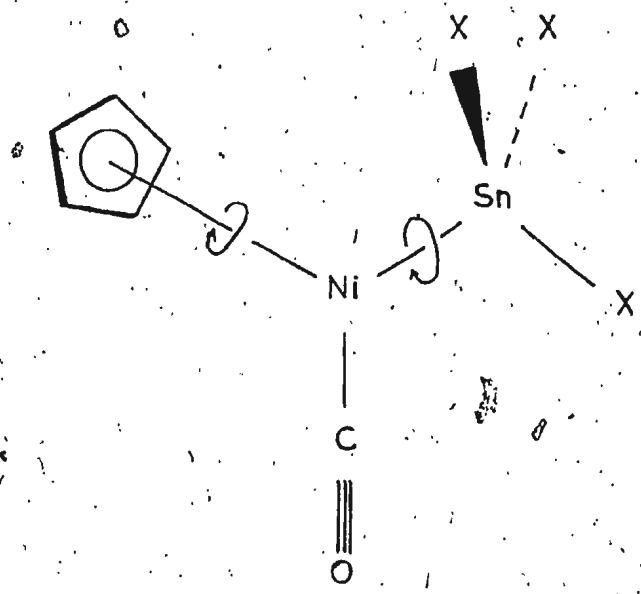
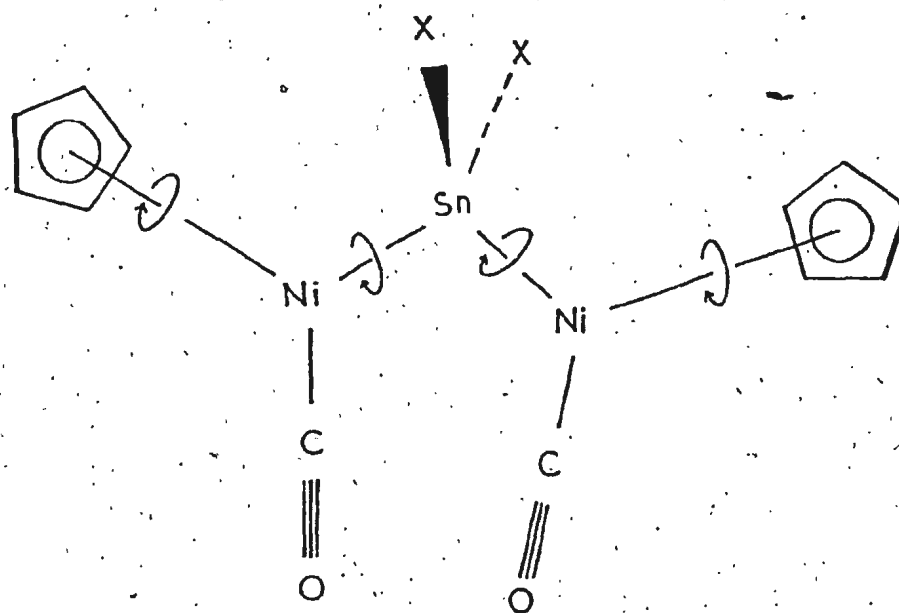


Fig. 3

Fig 4a

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Or

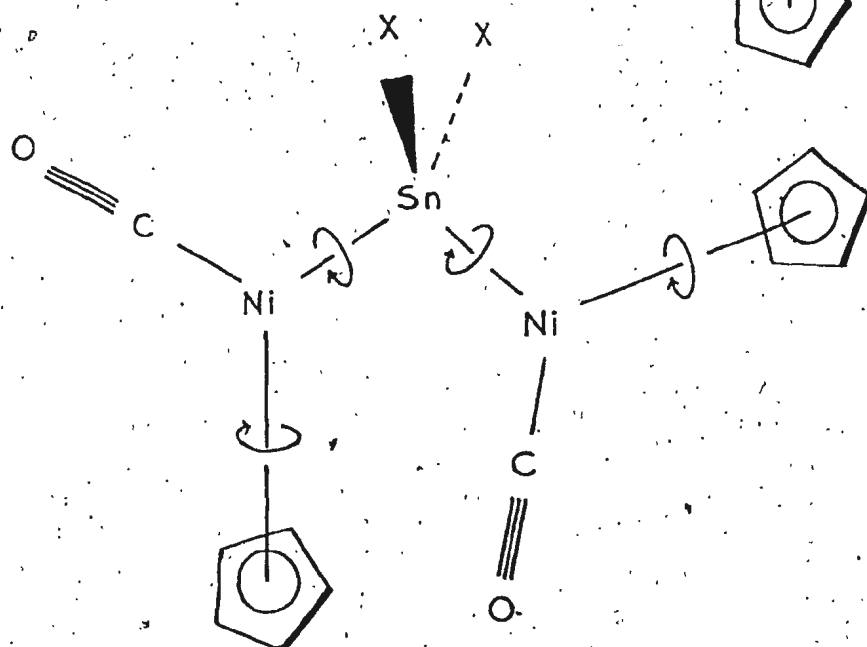
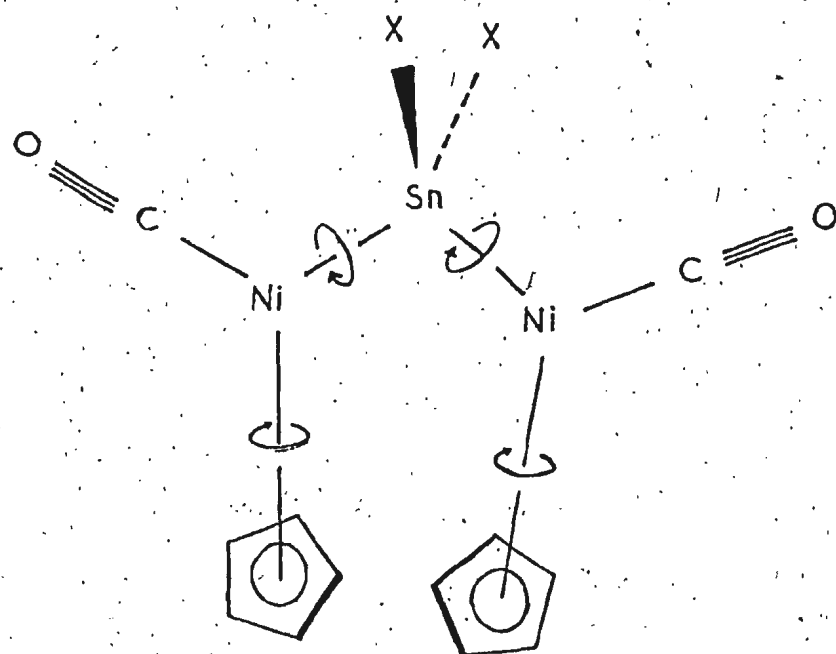


Fig. 4b

Fig. 4c

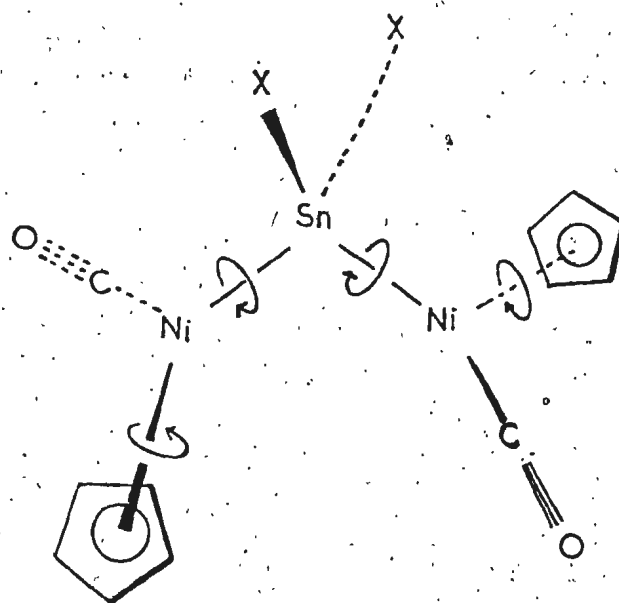
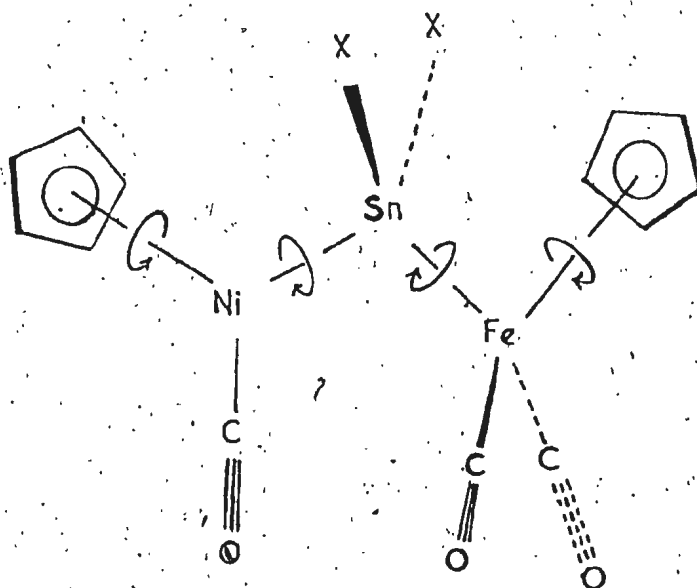


Fig. 5



The trigonal bipyramidal arrangement is in accordance with dsp^3 hybrid orbitals allowed by the electron arrangement about the nickel atom.

Probable structures of the complexes $(\pi-C_5H_5)Ni(CO)SnX_3$, $[(\pi-C_5H_5)Ni(CO)]_2SnX_2$, $(\pi-C_5H_5)Ni(CO)SnX_2(CO)_2Fe(\pi-C_5H_5)$ ($X = Cl, Br$) are shown in Figures 3, 4, and 5 respectively, following Table 2.

4. Infrared Spectra.

Infrared spectra of the complexes in solution show, respectively, one, two, or three strong or moderately strong absorptions in the terminal carbonyl stretching range ($1900-2100cm^{-1}$).

For the compounds $(\pi-C_5H_5)Ni(CO)SnX_3$ ($X = Cl, Br$), the single absorption band in the terminal stretching range is in accordance with the expected structure.

The presence of two terminal carbonyl stretching bands for the compounds $[(\pi-C_5H_5)Ni(CO)]_2SnX_2$ ($X = Cl, Br$) can be attributed to two vibrational modes: symmetric and antisymmetric (Figs. 4a, 4c) -- or simply: in phase, out of phase. Here, as in the case of the corresponding iron compounds,¹²⁶ the higher wavenumber is assumed to correspond to the symmetrical vibration.

In the heterotrimetallic derivatives, the bands can be assigned on the basis of local symmetry, provided no appreciable coupling between the carbonyl groups on the iron atom and the carbonyl group on the nickel atom is assumed. One band can be assigned to the C - O stretch at the nickel atom; the other two to symmetric and antisymmetric C - O stretches at the iron atom. (The group, $(\pi-C_5H_5)Fe(CO)_2$, has a plane of symmetry bisecting the angle between the two Fe - C $\equiv$ O bonds.)

Since the average C - O stretch in a compound of the type $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnX}_3$ occurs at a lower energy than the C - O stretch in a corresponding nickel compound, we may assign the highest energy C - O stretch to that of the group attached to the nickel atom, the next highest to the symmetric C - O stretch at the iron atom, and the lowest to the antisymmetric stretch at the iron atom.

The effect of the various substituents at the tin atom on the energy of the C - O stretching absorption in these compounds will be discussed later.

5. ^1H NMR Spectra.

The ^1H NMR spectra of the complexes show an interesting trend. Those complexes containing only one nickel group attached to the tin atom show a resonance of the cyclopentadienyl hydrogens in the region of τ 4.2, whereas those containing two transition metal groups show a resonance for the cyclopentadienylnickel hydrogens in the region of τ 4.4. (Since in the iron-tin compounds the resonances generally occur at higher τ values than those of the corresponding nickel-tin compounds, the resonance at the higher τ value in the heterotrimetallic compounds is assigned to the cyclopentadienyliron hydrogens while that at the lower τ value is assigned to the cyclopentadienylnickel hydrogens.)

A comparison of the NMR spectra of the compounds $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnCl}_3$ and $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnCl}_2$ ⁸⁴ shows the same contrast between compounds containing one or two transition metal groups attached to the same tin atom.

The effects of various substituents at the tin atom on the cyclopentadienyl hydrogen resonance in these compounds will be discussed

later in more detail when they will be considered along with effects on other physical parameters, notably the C - O stretching absorptions in the infrared spectra of the complexes.

6. Electronic Spectra.

Very little study has been done on the electronic spectroscopy of organometallic compounds with metal-metal bonds. To assign the absorption maxima of these compounds to particular electronic transitions would be beyond the scope of this work. However, some of the regularities observed in the electronic spectra of the compounds prepared here are worth noting.

All the complexes show an absorption at about 240nm and most show one at about 260-290nm. Most of the complexes also show a third absorption at about 300nm, and absorptions at longer wavelengths were noted in four of the complexes. For most of the complexes, three absorption maxima were observed, of which the peak at about 260-290nm was the most intense.

The number of transition metal groups, or the number or kind of halogen atoms attached to the tin atom did not affect the values of $\lambda_{\max}$ in any regular fashion except in the case of the compounds $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2\text{SnX}_2$. In this case, where $\text{X} = \text{Br}$, the values of $\lambda_{\max}$ were all shifted to a longer wavelength compared to where $\text{X} = \text{Cl}$.

Values of $\epsilon_{\max}$ were not calculated, as the solutions decomposed rapidly, making the calculated values unreliable. However, the relative intensities of the absorptions in each spectrum are noted, using the same notation as is common in infrared spectra.

Curiously, the colour of the heterotrimetallic complexes appeared

to be something between the colours of the iron-tin complexes and the nickel-tin complexes, although no such regularity was observed in the electronic spectra of these substances.

7. Mass Spectra.

Because of the large number of stable nuclides of nickel, and especially of tin, mass spectra of the complexes, which were difficult to obtain in good quality in any case, were in addition, difficult to interpret.

Figures 6, 7, 8, 9, overleaf, show, respectively, the patterns expected for ions containing Sn^+ , SnNi^+ , SnNi_2^+ , and SnNiFe^+ only. Since, in these compounds, chlorine or bromine is always present, many of the ions in the mass spectrometer contained atoms of these elements, thus making the patterns even more complicated.

Where iron was present in the compound, the patterns were not quite so complex, since over 90% of natural iron is ^{56}Fe .

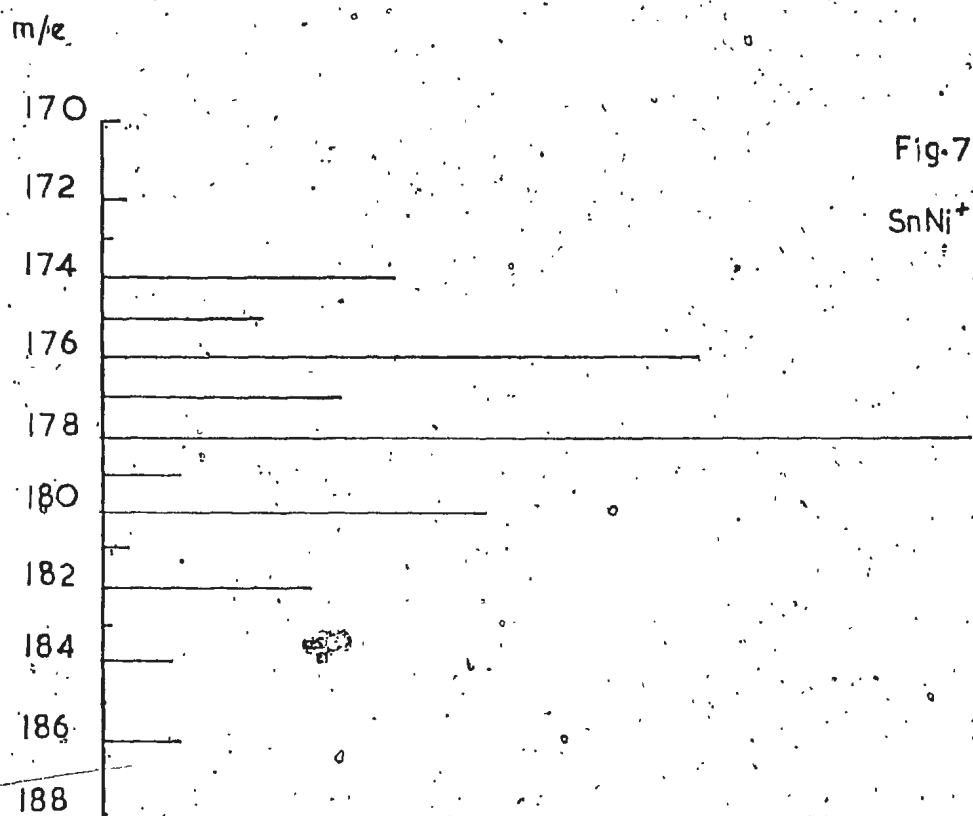
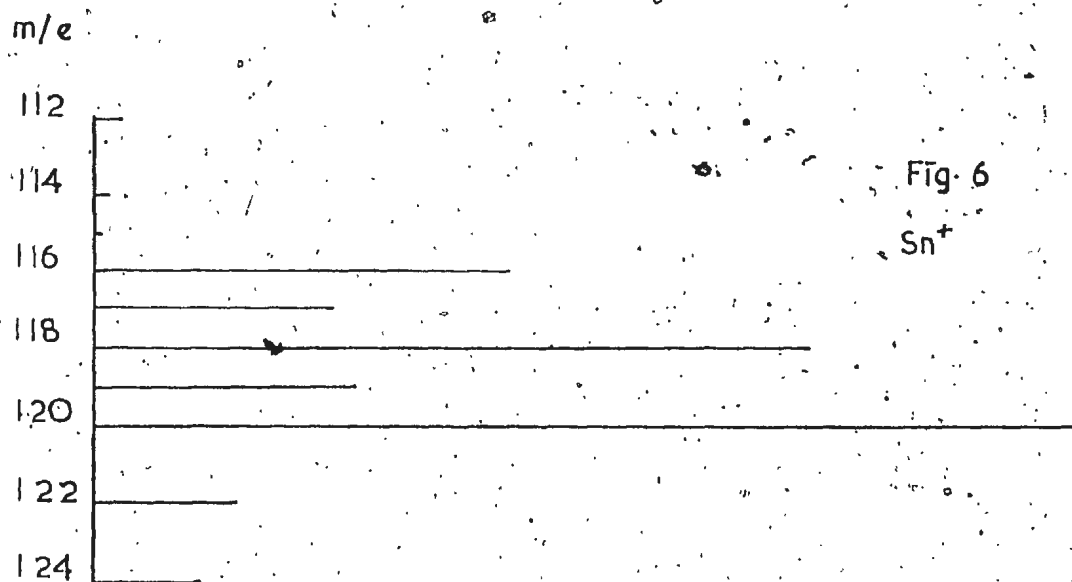
The parent ion, if its presence could be observed at all, was generally not very abundant (< 1%). Progressive loss of carbonyl groups could be seen in the spectra of all the compounds, except for $(\pi\text{-C}_5\text{H}_5)\text{-Ni(CO)SnBr}_3$, for which no spectrum containing fragments above m/e 200 could be obtained of good enough quality.

The most abundant ion had m/e values corresponding to the ion $(\text{C}_5\text{H}_5)_2\text{Ni}^+$, and this was present even where there was only one cyclopentadienyl group per molecule. This ion may be the result of ion-molecule collision inside the mass spectrometer. The next most abundant ion was $(\text{C}_5\text{H}_5)\text{Ni}^+$.

The m/e values of the most abundant ions suggest fragments in

FIGURES 6 - 9

THEORETICAL ISOTOPIC CONSTITUTIONS OF THE SKELETAL IONS IN MASS SPECTRA OF
POLYMETALLIC COMPOUNDS.



m/e

228

230

232

234

236

238

240

242

244

246

Fig. 8

 SnNi_2^+

m/e

224

226

228

230

232

234

236

238

240

242

244

Fig. 9

 SnNiFe^+

accordance with the proposed structures shown in Figures 3, 4 and 5.

What appeared to be metastable peaks were observed in the mass spectra of the compounds $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})]_2\text{SnBr}_2$ and $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})\text{SnCl}_3$ at m/e 188 and 123 in each case. Closer investigation revealed that these peaks did not correspond to any of the possible fragmentations for these compounds. Since there are a large number of very strong peaks at these m/e values, corresponding to $(\text{C}_5\text{H}_5)_2\text{Ni}^+$ and $\text{C}_5\text{H}_5\text{Ni}^+$, noise might well account for the observation.

8. General Trends in the Spectra.

The carbonyl stretching frequencies in the infrared spectra of the compounds synthesised here, together with the cyclopentadienyl hydrogen resonances in the ^1H NMR spectra, show some interesting trends.

If a chloride compound is compared with the corresponding bromide derivative, it is observed that, with the exception of the symmetric stretch in the heterotrimetallic compounds, the C - O stretch is at a higher energy in the chloride derivative. This suggests that $-\text{SnCl}_3$ is a better electron withdrawing group than $-\text{SnBr}_3$. The withdrawal of electron density from the transition metal atom weakens $d\pi - p\pi$ bonding between the transition metal and carbon atoms, and raises the C - O bond order, thus requiring higher energy for vibration. The same argument applies where $-\text{SnCl}_2$ is a better electron withdrawing group than $-\text{SnBr}_2$.

The ^1H NMR spectra of the compounds also support this argument. Comparison of corresponding chloro- and bromo- derivatives shows that resonances occur at lower τ values in the chloro- derivatives. The better electron withdrawing ability of $-\text{SnCl}_3$ (compared to $-\text{SnBr}_3$) or $-\text{SnCl}_2$ -

(compared to $-\text{SnBr}_2-$) leads to decreased electron density at the transition metal atom, weakening bonding between the transition metal and the cyclopentadienyl ring and decreasing the shielding of the ring protons.

Similar findings have been made in the series of compounds $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_n\text{SnX}_{4-n}$ ($\text{M} = \text{Mo}, \text{W}; n = 1, 2; \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{alkyl}, \text{Ph}, \text{NO}_2, \text{SC}_2\text{H}_5, \text{SCN}$),¹⁴⁴ the series $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_n\text{SnX}_{4-n}$ ($n = 1, 2; \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{alkyl}, \text{aryl}, \text{ONO}, \text{OCOCH}_3, \text{SC}_2\text{H}_5, \text{SCN}$)¹²⁶ with some anomalies, and the series $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).⁸⁴

If the compounds containing one nickel group are compared with those containing two nickel groups attached to the tin atom, it is observed that the carbonyl stretching absorptions in the infrared spectra are at lower energy in the latter group, with a difference in wavenumber of about $30\text{--}35\text{cm}^{-1}$ between the absorption in the monosubstituted compounds and the symmetric stretch in the disubstituted compounds. Also, the cyclopentadienyl hydrogen resonances in the ^1H NMR spectra are at lower τ values in the monosubstituted compounds, the difference being of the order of 0.2ppm .

The differences can be attributed to the need for the electron withdrawing effect of the tin-halogen group to be shared between the two nickel groups in the disubstituted compounds, and also to the presence of two, rather than three halogen atoms attached to the tin atom.

A comparison of the carbonyl stretching absorptions in the infrared spectra and the cyclopentadienyl hydrogen resonances in the ^1H NMR spectra of the heterotrimetallic compounds with those of either the monosubstituted nickel-tin or iron-tin compounds shows the same effect of

sharing the tin-halogen group. The values of ν_{C-O} and $\tau_{C_5H_5}$ for the compounds $(\pi-C_5H_5)Fe(CO)_2SnX_3$ ($X = Cl, Br$) are shown in Table 3, overleaf.

It is of interest to note here that the stabilities of the nickel compounds synthesised in this work appear to be related to the electron withdrawing ability of the tin-halogen group in each case. The least stable is $(\pi-C_5H_5)Ni(CO)SnCl_3$, in which the $-SnCl_3$ group is most electron-withdrawing. The next less stable is $(\pi-C_5H_5)Ni(CO)SnBr_3$, in which the $-SnBr_3$ group is only slightly less electron-withdrawing. Somewhat more stable is $[(\pi-C_5H_5)Ni(CO)]_2SnCl_2$, in which the electron-withdrawing ability of the $-SnCl_2-$ group must be shared by the two nickel groups, followed by $[(\pi-C_5H_5)Ni(CO)]_2SnBr_2$, in which the $-SnBr_2-$ group is only slightly less electron-withdrawing than $-SnCl_2-$. The iron-tin-nickel compounds are the most stable, for reasons not as yet clear.

Since electron withdrawal of the tin-halogen group lowers the electron density around the transition metal atom, the metal-carbon bonds are weakened, allowing cleavage of the π -bonded ligands. This is much the same as in the case of the transition metal carbonyl halides already discussed.

Because of the different number of carbonyl stretching bands in the infrared spectra of the compounds $[(\pi-C_5H_5)Ni(CO)]_2SnX_2$, $[(\pi-C_5H_5)Fe(CO)_2]_2SnX_2$, and $(\pi-C_5H_5)Ni(CO)SnX_2(CO)_2Fe(\pi-C_5H_5)$ ($X = Cl, Br$) -- two, four, and three respectively -- a direct comparison is not easy.

If, as previously stated, the highest energy carbonyl stretching absorption in an infrared spectrum of a heterotrimetallic compound is attributed to the nickel C - O stretch, then its energy is in much the same range as the carbonyl stretches in the dinickel-tin compounds, while the

TABLE 3

Physical Measurements on Previously Published Compounds.

Compound	ν_{C-O} (cm^{-1})	$\tau_{C_5H_5}^d$	References
$[(\pi-C_5H_5)Fe(CO)_2]_2SnCl_2$	2014s(sh), 2000s 1960s, 1934m(sh) ^a 2027s, 2000s, 1970s; 1958m(sh) ^b	4.93	88
$[(\pi-C_5H_5)Fe(CO)_2]_2SnBr_2$	2004s, 1998s(sh), 1964m, 1948s, 1932s(sh), 1920m(sh) ^a 2022s, 1998s 1971s, 1957m(sh) ^b	4.94	88
$(\pi-C_5H_5)Fe(CO)_2SnCl_3$	2055, 2000 2062vs, 1980vs ^a 2041, 2002 ^c	4.40 4.82	84 46 47 89
$(\pi-C_5H_5)Fe(CO)_2SnBr_3$	2045, 1996 2038, 1999 ^c	4.41 4.83	84 47 89

^aAs Nujol mull; NaCl plates^cAs CS₂ solution^bAs CHCl₃ solution in 0.5mm KBr cell^dAs CDCl₃ solution; TMS reference

absorptions due to the iron C - O stretches fall in much the same range as the more symmetric carbonyl stretches in the di-iron-tin compounds.

This evidence suggests that substituting an iron group for a nickel group or vice versa has little or no effect on the bond energies in the remaining transition metal group. Looked at another way, the electron donor properties of the groups $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ and $(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})$ seem to be much the same.

The ^1H NMR spectra of the compounds are slightly easier to interpret in this light. The cyclopentadienylnickel hydrogen resonance in the heterotrimetallic compounds is at a very slightly higher τ value (by 0.01 or 0.02ppm) than in the dinickel-tin compounds. The cyclopentadienyliron hydrogen resonances in the heterotrimetallic compounds are either up by 0.01ppm (in the case of the chloride) or down by 0.01ppm (in the case of the bromide), compared to the di-iron-tin compounds.

This suggests that the nickel group is marginally more electron-attracting than the iron group, if there is any difference at all, since an increase in τ value suggests less electron donation by the transition metal atom.

9. Possible Future Developments

In the field of organometallic compounds with metal-metal bonds, so much work has been done on the synthetic aspects that it seems there is not much more to be done in producing novel compounds except by using well-tried methods. However, some of the synthetic methods referred to in the Introduction to this thesis may enjoy wider use in future where it is desired to prepare compounds that have so far defied attempts at synthesis by other, better-known means.

There is a great need for a better understanding of the nature of the metal-metal bond. This may be achieved by further research into spectroscopic properties of metal-metal bonded complexes. For example, very little work has been done on the electronic spectra of these compounds. Also, photoelectron spectroscopy would be a useful tool in elucidating the nature of the bonding involved in these compounds. Studies of the reactions of these compounds would also be useful in shedding some light on the nature of the metal-metal bonds.

In some groups of these compounds there is a dearth of research into the crystal structures. To date, there have been no studies done on carbonyl- π -cyclopentadienylnickel derivatives, for example.

Some compounds similar to those prepared as part of the work of this thesis have been tested as anti-knock additives to hydrocarbon fuels or as additives to reduce wear in lubricants.²⁷ It is to be hoped that wider use may be found for these compounds.

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