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HETERONUCLEAR METAL–METAL BONDED COMPOUNDS

II*. IRON–GERMANIUM–NICKEL AND IRON–TIN–NICKEL BONDS

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SUMMARY

The reaction of substituted germanium and tin halides, $RGeX_3$, $RSnX_3$ ($X=Cl$, Br), where R is $CpFe(CO)_2$, with bis(carbonyl-π-cyclopentadienylnickel) has been found to provide a facile route to some novel heterotrimetallic systems, $CpFe(CO)_2MX_2Ni(CO)Cp$ ($M=Ge$, Sn; $X=Cl$, Br), containing Fe–Sn–Ni and Fe–Ge–Ni bonds.

INTRODUCTION

Metal–metal bonded organometallic systems containing nickel bonded to a Group IV element are not very numerous. A few bimetallic systems have been reported[1–8]. Of these the compounds $(C_5H_5)Ni(CO)MX_3$ ($M=Ge$; $X=Cl$, Br, I, $M=Sn$; $X=Cl$, Br and $M=Si$; $X=Cl$) are the only ones produced by reaction between a Group IV halide and the dimeric metallocarbonyl, bis(carbonyl-π-cyclopentadienylnickel). This type of reaction, previously reported by us[1,9], seems to be a versatile method for the production of metal–metal bonded compounds and has now been extended to produce novel heterotrimetallic systems containing two different transition elements bonded to a Group IV metal. In this study bis(carbonyl-π-cyclopentadienylnickel) has been reacted with substituted Group IV halides, *e.g.* $(C_5H_5)Fe(CO)_2MX_3$ ($M=Ge$, Sn; $X=Cl$, Br) with the formation of heterotrimetallic species containing a chain of three different metal atoms, Fe–M–Ni ($M=Ge$, Sn). Previously reported heterotrimetallic derivatives of this type involving Group IV metals bonded to nickel or iron contain a chain of three metal atoms in which the two transition elements are identical, [Fe–M–Fe ($M=Ge$, Sn) and Ni–M–Ni ($M=Ge$, Sn)][10–13].

DISCUSSION

Bis(dicarbonyl-π-cyclopentadienyliron) and bis(carbonyl-π-cyclopentadienyl-

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nickel) both react readily with germanium and tin tetrahalides in refluxing benzene with cleavage of the metal–metal bonds and subsequent formation of tin–iron, tin–nickel, germanium–iron and germanium–nickel bonds[1,9]. Reaction of $(C_5H_5)Fe(CO)_2SnX_3$ (X = Cl, Br) and $(C_5H_5)Fe(CO)_2GeX_3$ (X = Cl, Br) with $[(C_5H_5)Ni(CO)]_2$ in refluxing benzene gave the heterotrimetallic products containing iron–germanium–nickel and iron–tin–nickel bonds according to the following equation:

$$(C_5H_5)Fe(CO)_2MX_3 + [(C_5H_5)Ni(CO)]_2 \rightarrow$$

$$(C_5H_5)Fe(CO)_2MX_2Ni(CO)(C_5H_5) + (C_5H_5)Ni(CO)X$$

M = Sn, Ge ; X = Cl, Br

The products were obtained as dark green, somewhat air sensitive solids, which were stored under nitrogen in the absence of light. In each reaction a significant quantity of the trinuclear species $[(C_5H_5)Ni]_3(CO)_2$, was produced. This compound was identified by infrared[14] and mass spectroscopic data[15]. Other by-products, $(C_5H_5)Ni(CO)X$ and $(C_5H_5)_2Ni$, were also detected in the reaction mixtures by infrared and mass spectral data. According to Fischer and Palm[16] the compound $(C_5H_5)Ni(CO)I$ is unstable but can be isolated. The corresponding chloride and bromide compounds however appear to be far more unstable and could not be isolated from the reaction mixtures.

TABLE 1

ANALYTICAL AND OTHER DATA

Compound	*M.p. (°C)*	*Colour*	*Analysis found (calcd.) (%)*		
			C	*H*	*X (Cl, Br)*
$(C_5H_5)Fe(CO)_2GeCl_2Ni(CO)(C_5H_5)$	154–155	dark green	33.1 (33.1)	2.22 (2.12)	14.5 (15.0)
$(C_5H_5)Fe(CO)_2GeBr_2Ni(CO)(C_5H_5)$	141	dark green	28.0 (27.8)	1.95 (1.78)	27.9 (28.5)
$(C_5H_5)Fe(CO)_2SnCl_2Ni(CO)(C_5H_5)$[a]	>295 dec.	dark green	30.2 (30.2)	2.08 (1.95)	13.5 (13.7)
$(C_5H_5)Fe(CO)_2SnBr_2Ni(CO)(C_5H_5)$	>295 dec.	dark green	25.5 (25.8)	1.80 (1.67)	26.3 (26.3)

[a] This compound has been previously prepared by insertion of $SnCl_2$ into $(C_5H_5)Fe(CO)_2Ni(CO)(C_5H_5)$[18].

Analytical data are collected in Table 1 and infrared and ^1H NMR spectroscopic data in Table 2. The heterotrimetallic germanium derivatives exhibited melting points below 160° while the analogous tin compounds did not melt even at 295°, but showed significant decomposition with release of carbon monoxide.

Two singlet peaks of equal intensity are observed in the NMR spectrum of each compound, corresponding to protons on π-cyclopentadienyl rings bonded to both iron and nickel. By comparison with NMR data for known compounds (Table 3) it is possible to assign the low field peaks to protons on π-cyclopentadienyl rings bonded to nickel, while those at higher field strengths are assigned to protons on π-cyclopentadienyl rings bonded to iron.

TABLE 2

INFRARED AND NMR DATA

Compound	*ν(CO)* (*cm^{-1}*)	*τ(C_5H_5)*[c]
$(C_5H_5)Fe(CO)_2GeCl_2Ni(CO)(C_5H_5)$	2034 s, 2006 s(sh), 2002 s, 1961 s[a]	4.51, 5.04
	2042 s, 2016 s, 1972 s[b]	
$(C_5H_5)Fe(CO)_2GeBr_2Ni(CO)(C_5H_5)$	2034 ms, 2008 s, 1976 s[a]	4.49, 5.03
	2039 s, 2015 s 1973 s[b]	
$(C_5H_5)Fe(CO)_2SnCl_2Ni(CO)(C_5H_5)$	2028 s, 2007 ms, 1994 ms, 1960 ms[a]	4.43, 4.92
	2034 s, 2008 s, 1968 s[b]	
$(C_5H_5)Fe(CO)_2SnBr_2Ni(CO)(C_5H_5)$	2031 ms, 2003 s, 1964 s[a]	4.45, 4.96
	2035 s, 2006 s, 1968 ms[b]	

[a] Infrared spectra run as nujol mulls between sodium chloride plates.
[b] Infrared spectra run as $CHCl_3$ solutions in 0.5 mm KBr cells.
[c] Ref. TMS; in $CDCl_3$.

Mull infrared spectra of the complexes $[(C_5H_5)Fe(CO)_2]_2SnX_2$ (X = Cl, Br) (Table 3) exhibit their highest energy CO stretching bands around 2000 cm^{-1} whereas for the complexes $[(C_5H_5)Ni(CO)]_2MCl_2$ (M = Sn, Ge) (Table 3) the highest energy CO stretching absorptions occur around 2030 cm^{-1}. In solution in chloroform a similar trend is observed, the nickel complexes having their highest energy CO stretching absorptions 15 cm^{-1} or more to higher energies than the iron complexes. These data suggest a greater reluctance on the part of the $(C_5H_5)Fe(CO)_2$ groups to give up electron density to the electron-withdrawing MX_2 groups. This is substantiated by the NMR data, which indicate a greater electron withdrawal from the π-cyclopentadienyl rings in the case of the heterotrimetallic nickel complexes.

The complexes $[(C_5H_5)Fe(CO)_2]_2SnX_2$ (X = Cl, Br) exhibit slight splitting of the band above 2000 cm^{-1} in the solid state which is markedly enhanced in solution in chloroform, where the splitting approaches 25 cm^{-1}. In both complexes four bands are observed in solution, which could be expected for a system containing two non-equivalent $(C_5H_5)Fe(CO)_2$ groups.

In the case of the nickel compounds very little difference is observed between the solid and solution spectra. In solution the CO absorptions are shifted to higher energies by about 10 cm^{-1}.

A comparison of the CO stretching absorptions in the solution spectra of the

TABLE 3

INFRARED AND NMR DATA OF PREVIOUSLY PUBLISHED HETEROTRIMETALLIC SYSTEMS (all IR and NMR data remeasured.)

Compound	*ν(CO)* (*cm*$^{-1}$)	*τ*(C_5H_5) (*solvents*)[c]	*Ref.*
$[(C_5H_5)Fe(CO)_2]_2SnCl_2$	2014 s(sh), 2000 s, 1960 s, 1934 m(sh)[a]	4.93 ($CDCl_3$)	9, 13, 17
	2027 s, 2000 s, 1970 s, 1958 m(sh)[b]		
$[(C_5H_5)Fe(CO)_2]_2SnBr_2$	2004 s, 1998 s(sh), 1964 m, 1948 s, 1932 s(sh), 1920 m(sh)[a]	4.94 ($CDCl_3$)	10
	2022 s, 1998 s, 1971 s, 1957 m(sh)[b]		
$[(C_5H_5)Ni(CO)]_2SnCl_2$	2038 s(sh), 2029 s[a]	4.45	10
	2042 s, 2032 s(sh)[b]	($CDCl_3$)	
$[(C_5H_5)Ni(CO)]_2GeCl_2$	2036 s(sh), 2024 s 1988 w[a]	4.46 ($CDCl_3$)	1
	2044 s(sh), 2034 s[b]		
$[(C_5H_5)Ni(CO)]_2SnBr_2$	2030 s, 2019 mw[a]	4.43 ($CDCl_3$)	1

[a] Infrared spectra run as nujol mulls between sodium chloride plates.
[b] Infrared spectra run as $CHCl_3$ solutions in 0.5 mm KBr cells.
[c] Ref. TMS.

mixed trimetallic systems with those of the iron trimetallics and the nickel trimetallics and previously reported bimetallic systems $(C_5H_5)Fe(CO)_2MX_3$[1,9,13] (M=Ge, Sn; X=Cl, Br) and $(C_5H_5)Ni(CO)MX_3$[1] (M=Ge, Sn; X=Cl, Br) indicates that the spectral bands can be divided into two types. The highest energy band in each case can be associated with the $(C_5H_5)Ni(CO)$ group while the two lower bands can be assigned to the symmetric and asymmetric CO stretch associated with the $(C_5H_5)Fe(CO)_2$ groups. As would be expected, all the CO absorptions appear at lower energies than in the corresponding bimetallic systems, as a result of the reduced electron-withdrawing characteristics of the bridging MX_2 group in comparison with the terminal MX_3 group. However it appears that the two metallocarbonyl groups are behaving independently in the heterotrimetallic compounds.

The heterotrimetallic chloride complexes exhibit absorptions in the solid state, around 2000 cm^{-1}, which are split into two distinct bands. Such splitting is not observed in the case of the same absorption in the analogous bromide complexes. In solution however, the doublet absorptions are observed to coalesce and a singlet is observed shifted to higher energies for each of the chloride complexes. This suggests the possible presence of differing site symmetries in the solid state which are destroyed in favour of an averaged situation in solution. The most pronounced splitting of the

CO absorption in question occurs with the complex $(C_5H_5)Fe(CO)_2SnCl_2Ni(CO)(C_5H_5)$. A less marked splitting occurs with the $GeCl_2$ complex while no apparent splitting is observed for the $GeBr_2$ and $SnBr_2$ complexes.

The NMR spectra of the mixed trimetallic systems indicate very little difference in the chemical shifts associated with the π-cyclopentadienyl ring protons bonded to nickel and iron when compared with such complexes as $[(C_5H_5)Ni(CO)]_2MCl_2$ (M=Sn, Ge) and $[(C_5H_5)Fe(CO)_2]_2SnX_2$ (X=Cl, Br). This indicates, along with the infrared data, that the bridging groups MX_2 (M=Ge, Sn; X=Cl, Br) are not as efficient in their electron-withdrawing characteristics as MX_3[1,9] groups and do not provide a suitable pathway for charge transfer between the two organometallic groups.

TABLE 4

MASS SPECTRAL DATA

$(C_5H_5)Fe(CO)_2GeCl_2Ni(CO)(C_5H_5)$			$(C_5H_5)Fe(CO)_2GeBr_2Ni(CO)(C_5H_5)$		
m/e	*Assignment*	*Inlet temp.*	*m/e*	*Assignment*	*Inlet temp.*
444	$P-CO$	250°	534	$P-CO$	230°
416	$P-(CO)_2$		506	$P-(CO)_2$	
388	$P-(CO)_3$		478	$P-(CO)_3$	

$(C_5H_5)Fe(CO)_2SnCl_2Ni(CO)(C_5H_5)$			$(C_5H_5)Fe(CO)_2SnBr_2Ni(CO)(C_5H_5)$		
m/e	*Assignment*	*Inlet temp.*	*m/e*	*Assignment*	*Inlet temp.*
518	P	230°	608	P	245°
490	$P-CO$		580	$P-CO$	
462	$P-(CO)_2$		552	$P-(CO)_2$	
434	$P-(CO)_3$				

Mass spectra were obtained using the direct insertion probe at temperatures of 230–250° and an ionizing beam of 70 eV. Mass spectral data are tabulated in Table 4. Only those peaks associated with loss of CO from the parent ion have been recorded since for the two germanium derivatives the operating probe temperature was greater than the melting point. In the case of the two germanium derivatives peaks due to the molecular ion are not observed but peaks due to removal of three successive CO groups are observed. $P-CO$ is the most intense peak in each case. The two tin derivatives do exhibit very weak molecular ion peaks and peaks due to successive removal of CO groups. Once again $P-CO$ is the most intense peak.

EXPERIMENTAL

All solvents were dried and degassed before use and all preparations and recrystallisations were carried out in "Airless Ware" apparatus in a dry nitrogen atmosphere.

Elemental analyses were carried out by the Alfred Bernhardt Microanalytical Laboratories, West Germany. IR spectra were recorded on a Perkin–Elmer Model 457. Calibration standards of DCl and polystyrene were employed in the range 2200–1900 cm^{-1}. NMR spectra were recorded on a Varian A60 instrument. Mass spectra were obtained using a Perkin–Elmer–Hitachi RMU-6E instrument with the direct insertion probe. Analytical and other data are recorded in Table 1.

(1) *(Dicarbonyl-π-cyclopentadienyliron)(carbonyl-π-cyclopentadienylnickel) dibromogermanium(IV)*

(Dicarbonyl-π-cyclopentadienyliron)tribromogermanium(IV)[1] (1.00 g, 2.04 mmole) and bis(carbonyl-π-cyclopentadienylnickel) (0.70 g, 2.30 mmole) were mixed together in dry oxygen-free benzene (50 ml) and the mixture was refluxed under nitrogen for 6 h. During this time the disappearance of the bridging carbonyl group in $[CpNi(CO)]_2$ was monitored using infrared spectroscopy. The solvent was removed under vacuum leaving a dark black-brown solid. A small quantity of green crystals of nickelocene was observed to volatilise from the solid product on evacuating to dryness. The dark solid was extracted into dichloromethane/hexane (50/50) and filtered under nitrogen. The extract was concentrated and cooled leaving dark brown-green crystals, which were filtered, washed with hexane and dried under vacuum. Recrystallisation was effected using the same solvent mixture to give (dicarbonyl-π-cyclopentadienyliron) (carbonyl-π-cyclopentadienylnickel) dibromogermanium (IV) (0.68 g, 1.2 mmoles, 59%).

The compounds $(C_5H_5)Fe(CO)_2GeCl_2Ni(CO)(C_5H_5)$ (10%), $(C_5H_5)Fe(CO)_2SnCl_2Ni(CO)(C_5H_5)$ (65%) and $(C_5H_5)Fe(CO)_2SnBr_2Ni(CO)(C_5H_5)$ (55%) were prepared similarly. Longer reflux times were required for the chloride complexes and the extent of reaction in each case was monitored by observing the disappearance of the bridging carbonyl group in bis(carbonyl-π-cyclopentadienylnickel) in the infrared. Significant quantities of nickelocene and the trinuclear nickel compound $[(C_5H_5)Ni]_3(CO)_2$ were observed in each reaction, probably as a result of decomposition of $[(C_5H_5)Ni(CO)]_2$. Bis(carbonyl-π-cyclopentadienylnickel) can be converted into the trimeric species simply by refluxing in benzene over an extended period of time.

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