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HETERONUCLEAR METAL–METAL BONDED COMPOUNDS I*. IRON–GERMANIUM, NICKEL–GERMANIUM, AND NICKEL–TIN BONDS

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SUMMARY

The reaction of germanium(IV), tin(II) and tin(IV) halides with bis(dicarbonyl-π-cyclopentadienyliron) and bis(carbonyl-π-cyclopentadienylnickel) has been used to prepare $CpFe(CO)_2GeX_3$ (X = Cl, Br, and I), $CpNi(CO)MX_3$ (M = Ge, X = Cl, Br, and I; M = Sn, X = Cl, Br) and $[CpNi(CO)]_2MX_2$ (M = Ge, X = Cl; M = Sn, X = Br).

INTRODUCTION

Several methods are available for the general synthesis of compounds containing metal–metal bonds (see for example ref. 1). A new method for the synthesis of heteronuclear metal–metal bonded compounds was introduced by one of us[2]. This method, which has seen little use, involves the reaction of a dimeric metal carbonyl with a metal halide, *e.g.*:

$$[CpFe(CO)_2]_2 + SnCl_4 \rightarrow CpFe(CO)_2SnCl_3 + CpFe(CO)_2Cl$$

The present work is part of a larger study to determine the range of utility of this type of reaction for the synthesis of compounds containing heteronuclear metal–metal bonds.

DISCUSSION

Germanium(IV) halides react with both bis(dicarbonyl-π-cyclopentadienyliron) and bis(carbonyl-π-cyclopentadienylnickel) in benzene solution as shown in eqn. (1):

$$[CpM(CO)_n]_2 + GeX_4 \rightarrow CpM(CO)_nGeX_3 + CpM(CO)_nX \quad (1)$$
$$(M = Fe,\ n = 2,\ X = Cl, Br, I;\ M = Ni,\ n = 1,\ X = Cl, Br, I)$$

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Tin(IV) halides react with bis(carbonyl-π-cyclopentadienylnickel) in benzene solution as shown in eqn. (2):

$$[CpNi(CO)]_2+SnX_4 \rightarrow CpNi(CO)SnX_3+CpNi(CO)X \qquad (2)$$

$$(X=Cl, Br)$$

The reactions with both iron and nickel dimers and germanium and tin tetrahalides involve rupture of a metal–metal bond and two bridging carbonyl groups and then the formation of two products, one involving a metal–metal bond and the other a metal–halogen bond. The iron–halogen bonded products, $(C_5H_5)Fe(CO)_2X$, are relatively stable and could be isolated by chromatographic techniques; the nickel–halogen bonded products, $(C_5H_5)Ni(CO)X$, were not isolated. According to Fischer and Palm the iodide is unstable[3]. In the nickel reactions significant quantities of a dark insoluble material containing nickel and no CO groups, were obtained. A new insertion product, $[CpNi(CO)]_2SnBr_2$, has been prepared by reaction of tin(II) bromide with bis(carbonyl-π-cyclopentadienylnickel) in refluxing THF. The iron compounds are obtained as yellow or brown, air-stable products from refluxing benzene. The nickel compounds are varying shades of green. They appear to be slowly oxidized in the dry state and the germanium iodide compound appears to be photosensitive. Both sets of compounds are oxidized slowly in solution. Analytical data are collected in Table 1 and infrared and ^1H NMR spectroscopic data in Table 2.

TABLE 1

ANALYTICAL AND OTHER DATA

Compound	M.p. (°C)	Colour	Analysis, found (calcd.) (%)		
			C	H	X
$(C_5H_5)Fe(CO)_2GeCl_3$	139	Yellow	24.0 (23.6)	1.7 (1.4)	30.0 (29.9)
$(C_5H_5)Fe(CO)_2GeBr_3$	158	Yellow	17.3 (17.2)	1.3 (1.0)	48.9 (49.0)
$(C_5H_5)Fe(CO)_2GeI_3$	145–147	Brown	13.6 (13.3)	0.8 (0.8)	60.0 (60.4)
$(C_5H_5)Ni(CO)GeCl_3$	73–75	Dark green	21.8 (21.8)	1.6 (1.5)	31.9 (32.1)
$(C_5H_5)Ni(CO)GeBr_3$	100–102	Dark green	15.5 (15.5)	1.2 (1.1)	51.6 (51.6)
$(C_5H_5)Ni(CO)GeI_3$	120–125	Dark green	12.0 (11.9)	1.0 (0.8)	63.2 (63.0)
$[(C_5H_5)Ni(CO)]_2GeCl_2$	109	Green	31.9 (32.1)	2.6 (2.2)	16.1 (15.9)
$(C_5H_5)Ni(CO)SnCl_3$	42–43 (dec.)	Green	18.9 (19.1)	1.4 (1.3)	28.3 (28.2)
$(C_5H_5)Ni(CO)SnBr_3$	56 (dec.)	Green	14.0 (14.1)	1.1 (1.0)	47.1 (47.2)
$[(C_5H_5)Ni(CO)]_2SnBr_2$	107–108	Green	24.8 (24.8)	1.9 (1.7)	27.4 (27.2)

TABLE 2

INFRARED AND NMR DATA

Compound	ν(CO)[a] (cm^{-1})	$\tau(C_5H_5)$[b]
$(C_5H_5)Fe(CO)_2GeCl_3$	2048 s, 2002 s(d)	4.78
$(C_5H_5)Fe(CO)_2GeBr_3$	2043 s, 2001 s(d)	4.83
$(C_5H_5)Fe(CO)_2GeI_3$	2041 s, 2001 s(d)	4.88
$(C_5H_5)Ni(CO)GeCl_3$	2075 s 2076 s, 2027 w[c](e)	4.25
$(C_5H_5)Ni(CO)GeBr_3$	2072 s 2074 s, 2024 w[c](e)	4.27
$(C_5H_5)Ni(CO)GeI_3$	2063 s	4.38
$(C_5H_5)Ni(CO)SnCl_3$	2072 s	4.18
$(C_5H_5)Ni(CO)SnBr_3$	2065 s, 2016 w[c]	4.23
$[(C_5H_5)Ni(CO)]_2GeCl_2$	2048 s(sh), 2039 s, 2024 s, 1988 w	4.46
$[(C_5H_5)Ni(CO)]_2SnBr_2$	2030 s, 2019 mw	4.43

[a] Infrared spectra run as nujol mulls between sodium chloride plates unless otherwise indicated. (d) in CH_2Cl_2; (e) in n-hexane. [b] Ref. TMS; in $CDCl_3$. [c] ^{13}C–O stretching frequency.

The reactions were monitored in the infrared by following the disappearance of the bridging carbonyl frequencies in the initial carbonyls. Because all the reactions were run under similar conditions it was possible to observe qualitatively that; (*i*) germanium(IV) chloride reacted more slowly than the other germanium halides, and (*ii*) that germanium(IV) chloride reacted more slowly than tin(IV) chloride. A further interesting observation is that the reaction between germanium(IV) chloride and the nickel dimer gave bis(carbonyl-π-cyclopentadienylnickel)germanium dichloride in addition to the monosubstituted product. It appears likely that the disubstituted product arose by reaction of the monosubstituted product with a further molecule of nickel dimer [eqn. (3)]:

$$CpNi(CO)GeCl_3 + [CpNi(CO)]_2 \rightarrow [CpNi(CO)]_2GeCl_2 + CpNi(CO)Cl \quad (3)$$

Other routes to the disubstituted product, *e.g.* reduction of $GeCl_4$ to $GeCl_2$ and then insertion into the nickel dimer[4] or into a Ni–Cl bond[5], seem unlikely.

The monosubstituted metal–metal bonded systems exhibit fairly high energy terminal CO stretching frequencies in the infrared. The iron compounds are characterised by two sharp carbonyl absorptions while the nickel compounds are characterised by one. These CO absorptions occur some 30–40 cm^{-1} higher than in the case of the corresponding methyl derivatives*. This suggests significant electron withdrawal from the iron and nickel atoms by the MX_3 groups. The trends within each group of trihalides indicate that the electron withdrawing ability of the MX_3 groups decreases as follows: $SnCl_3^- > SnBr_3^-$; $GeCl_3^- > GeBr_3^- > GeI_3^-$.

The disubstituted nickel systems exhibit up to four CO bands at lower energies. The MX_2 groups, bonded to two nickel atoms, exert a smaller electron withdrawing effect per nickel atom than the MX_3 groups.

All the metal–metal bonded systems exhibit single sharp peaks in the NMR.

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* $C_5H_5Ni(CO)CH_3$[6]: ν(CO) 2036; $C_5H_5Fe(CO)_2CH_3$[7]: ν(CO) 2010, 1955 cm^{-1}.

In the disubstituted sytems the two cyclopentadiene rings appear to be equivalent. For the monosubstituted systems the cyclopentadienyl hydrogen chemical shifts indicate a decrease in the electron withdrawing ability of the MX_3 groups as follows; $SnCl_3^- > SnBr_3^-$; $GeCl_3^- > GeBr_3^- > GeI_3^-$. The higher chemical shifts exhibited by the disubstituted nickel compounds parallel the infrared data. Electron withdrawal from the cyclopentadiene rings in the disubstituted systems is less than that in the monosubstituted systems.

EXPERIMENTAL

All solvents were dried and degassed before use. Benzene was stored over sodium and tetrahydrofuran stored over sodium benzophenone ketyl. In reactions involving the use of THF the solvent was distilled under vacuum into the reaction flask. All preparations and recystallisations were carried out in a dry nitrogen atmosphere.

Elemental analyses were carried out by the Alfred Bernhardt Microanalytical Laboratories, West Germany. IR spectra were recorded on Perkin–Elmer models 457 and 225. Calibration standards of polystyrene and CO_2 were employed in the range 2350–1900 cm^{-1}. NMR spectra were recorded on a Varian A60 instrument. Analytical data are recorded in Table 1.

1. *(Dicarbonyl-π-cyclopentadienyliron)trichlorogermanium(IV)*

Germanium tetrachloride (5 ml, 9.35 g, 43.5 mmole) and bis(dicarbonyl-π-cyclopentadienyliron) (5.0 g, 14 mmole) were mixed together in dry, oxygen-free benzene (300 ml) and the mixture was refluxed under nitrogen for 21 h. The solvent was removed under vacuum and the residue extracted with ether. Concentration of the ether extract and addition of petroleum ether (b.p. 40–60°) gave yellow crystals, which were recrystallised from ether/petroleum ether (b.p. 40–60°) to give (dicarbonyl-π-cyclopentadienyliron)trichlorogermanium(IV) (2.3 g, 6.5 mmole, 46 %) m.p. 139°. The remaining ether extract was concentrated and chromatographed on neutral alumina using petroleum ether (b.p. 40–60°) to yield red crystals of dicarbonyl-π-cyclopentadienyliron chloride (0.6 g, 2.8 mmole, 20 %). The compounds (dicarbonyl-π-cyclopentadienyliron)tribromogermanium(IV) (yield 66 %) and (dicarbonyl-π-cyclopentadienyliron)triiodogermanium(IV) (yield 32 %) were obtained by the same procedure. In both cases however, reflux times of 1 h only were required.

2. *(Carbonyl-π-cyclopentadienylnickel)trichlorogermanium(IV)*

Germanium tetrachloride (2 ml, 3.68 g, 17.1 mmole) and bis(carbonyl-π-cyclopentadienylnickel) (0.8 g, 2.75 mmole) were mixed together in dry, oxygen-free benzene (60 ml) and refluxed under nitrogen for 30 h. The dark green solution was cooled, filtered and its volume reduced to about 20 ml. Dropwise addition of hexane, under nitrogen, gave small green crystals which were identified as the disubstituted insertion-type product, $[(C_5H_5)Ni(CO)]_2GeCl_2$ (0.3 g, 0.67 mmole, 49 %) m.p. 109°. Concentration of the green filtrate and further dropwise addition of hexane gave large, dark green crystals which were recrystallised from CH_2Cl_2/hexane to give (carbonyl-π-cyclopentadienylnickel)trichlorogermanium(IV) (0.3 g, 0.91 mmole, 33 %) m.p. 73–75°. The compound (carbonyl-π-cyclopentadienylnickel)tribromogermanium(IV) was obtained by a similar procedure (yield 81 %). In this case though the reactants were stirred together at room temperature in benzene, under nitrogen, for 5 h prior to work-up. No disubstituted product was obtained.

3. *(Carbonyl-π-cyclopentadienylnickel)triiodgermanium(IV)*

Germanium tetraiodide (3.0 g, 5.15 mmole) and bis(carbonyl-π-cyclopentadienylnickel) (1.3 g, 4.3 mmole) were stirred together in dry, oxygen-free benzene (60 ml), at room temperature under nitrogen for 1½ h. The resulting dark green solution was filtered under nitrogen and allowed to stand at room temperature for 24 h. The dark solution was filtered again, the volume reduced to 20 ml and a few ml n-hexane added. Dark green, almost black crystals were obtained on cooling, which were recrystallised from benzene/hexane to give (carbonyl-π-cyclopentadienylnickel)triiodogermanium(IV) (1.5 g, 2.48 mmole, 58 %) m.p. 120–125°.

4. *(Carbonyl-π-cyclopentadienynickel)trichlorotin(IV)*

Tin tetrachloride (0.4 ml, 0.9 g, 3.5 mmole) and bis(carbonyl-π-cyclopentadienylnickel) (1.0 g, 3.3 mmole) were mixed in dry, oxygen-free benzene (30 ml) and stirred at room temperature under nitrogen for 40 min. The resulting green solution was filtered under nitrogen and its volume reduced to 10 ml and an equal volume of hexane added under nitrogen. Dark green needles were obtained which were recrystallised from benzene/hexane to give (carbonyl-π-cyclopentadienylnickel)trichlorotin-(IV) (0.46 g, 1.2 mmole, 37 %) m.p. 42–43° (dec.).

The compound (carbonyl-π-cyclopentadienylnickel)tribromotin(IV) was obtained by the same procedure. A reaction time of 1 h at room temperature was required (yield 36 %).

5. *Bis(carbonyl-π-cyclopentadienylnickel)dibromotin(IV)*

Anhydrous tin(II) bromide (1.0 g, 3.5 mmole) and bis(carbonyl-π-cyclopentadienylnickel) (0.62 g, 2.1 mmole) were refluxed together in dry, oxygen-free THF (50 ml) under nitrogen for 2 h. The solvent was removed under vacuum and the product extracted with chloroform. The green solution was reduced in volume and cooled to −60° to give dark green plates of bis(carbonyl-π-cyclopentadienylnickel)-dibromotin(IV) (0.62 g, 2.1 mmole, 53 %) m.p. 107–108°. The product was recrystallised from $CHCl_3$/hexane.

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