

NEW NICKEL-COBALT, NICKEL-IRON AND NICKEL-MANGANESE POLYNUCLEAR CARBONYL COMPLEXES

A. T. T. HSIEH AND J. KNIGHT

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

(Received July 30th, 1970)

SUMMARY

The new complexes $\pi\text{-C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9$, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ and $[\text{Me}_4\text{N}][(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]$ have been isolated from the reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Co}_2(\text{CO})_8$, $\text{Fe}_2(\text{CO})_9$ and $\text{Mn}(\text{CO})_5^-$ respectively, and have been characterised by analysis, IR, NMR, mass and Mössbauer spectroscopy. Probable structures for these compounds are discussed on the basis of their IR spectra. The reactions of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with other metal carbonyl species have been investigated.

INTRODUCTION

Although $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ has been known for a considerable time, its chemistry, compared with that of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ or $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$, has received little attention. We have now investigated its reactions with a number of metal carbonyls and report here the synthesis and characterisation of three new polynuclear carbonyl complexes $\pi\text{-C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9$, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ and $[\text{Me}_4\text{N}][(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]$.

Known polynuclear carbonyl complexes of nickel include homonuclear clusters such as $\text{Ni}_4(\text{CO})_9^{2-}$ and $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2^2$, as well as heteronuclear complexes such as $(\pi\text{-C}_5\text{H}_5)_2\text{NiFe}(\text{CO})_3^{3,4}$, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{PhC}_2\text{Ph})\text{Fe}(\text{CO})_3^4$, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{PhC}_2\text{Ph})\text{Fe}_2(\text{CO})_6^4$, $\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})(\text{PPh}_2)\text{Fe}(\text{CO})_3^5$, $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_2\text{Co}(\text{CO})_2^{6,7}$ and $\text{Ni}_2\text{Co}_4(\text{CO})_{14}^{2-8}$.

RESULTS AND DISCUSSION

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Co}_2(\text{CO})_8$

The reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Co}_2(\text{CO})_8$ in light petroleum gives, after chromatography, the green crystalline complex $\pi\text{-C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9$. Its identity was established by mass spectroscopy and verified by analysis. It is readily soluble in organic solvents and is slowly decomposed by air in the solid state and more rapidly in solution.

In its NMR spectrum, a singlet resonance due to the five equivalent cyclopent-

tadienyl protons is observed, whose chemical shift is similar to that of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$, indicating that the cyclopentadienyl group remains bonded to the nickel atom.

The mass spectrum of the complex shows the molecular ion, $\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9^+$, together with ions formed by loss of carbonyl groups (Table 1). At a low source temperature ($\sim 70^\circ$), a simple spectrum is observed and the ions $\text{C}_5\text{H}_5\text{Co}(\text{CO})_n^+$ ($n =$

TABLE 1

MONOISOTOPIC MASS SPECTRUM OF $\pi\text{-C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9^a$

Ion	m/e	Relative intensity	
		Source temp. $\sim 70^\circ$	Source temp. $\sim 110^\circ$
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9^+$	552	4.2	~ 0.1
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_8^+$	524	1.7	~ 0.1
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_7^+$	496	2.2	0.3
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_6^+$	468	0.7	0.3
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_5^+$	440	3.1	1.0
$\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})_7^+$	437		0.3
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_4^+$	412	3.2	2.9
$\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})_6^+$	409		0.5
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_3^+$	384	2.4	4.4
$\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})_5^+$	381		1.3
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})_2^+$	356	2.0	3.1
$\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})_4^+$	353		2.9
$\text{C}_5\text{H}_5\text{NiCo}_3(\text{CO})^+$	328	1.3	8.8
$\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})_3^+$	325		3.4
$\text{C}_5\text{H}_5\text{NiCo}_3^+$	300	2.5	40.5
$\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})_2^+$	297		9.6
$\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})^+$	269		14.6
$\text{C}_5\text{H}_5\text{NiCo}_2^+$	241	2.8	68.2
NiCo_3^+	235		4.2
$\text{C}_5\text{H}_5\text{NiCo}^+$	182		27.0
$\text{C}_5\text{H}_5\text{Co}(\text{CO})_2^+$	180	31.3	12.2
NiCo_2^+	176		25.0
$\text{C}_5\text{H}_5\text{Co}(\text{CO})^+$	152	39.1	8.0
$\text{C}_5\text{H}_5\text{Co}^+$	124	100	100

Metastable transitions

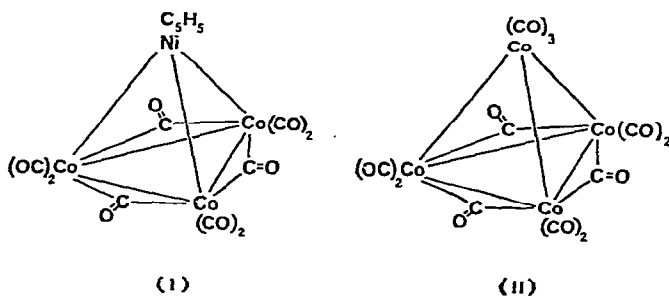
Process	m/e	
	Calcd.	Observed
$\text{C}_5\text{H}_5\text{NiCo}_3^+ \rightarrow \text{C}_5\text{H}_5\text{NiCo}_2^+ + \text{Co}$	193.6	194
$\text{C}_5\text{H}_5\text{Co}(\text{CO})_2^+ \rightarrow \text{C}_5\text{H}_5\text{Co}(\text{CO})^+ + \text{CO}$	128.4	128.4
$\text{C}_5\text{H}_5\text{Co}(\text{CO})^+ \rightarrow \text{C}_5\text{H}_5\text{Co}^+ + \text{CO}$	101.2	101.2

^a Taken at a source pressure of 2×10^{-7} mm. The characteristic isotope pattern was observed for each ion.

0–2) are the most abundant peaks in the spectrum. However, at a higher source temperature ($\sim 110^\circ$), additional ions such as $\text{C}_5\text{H}_5\text{NiCo}_2(\text{CO})_n^+$ ($n=0-7$), formed by loss of both carbonyl groups and cobalt metal atoms, are observed.

The presence of both terminal and bridging carbonyl groups in the complex is indicated by its IR spectrum. The only likely arrangement without violation of the eighteen-electron rule is the tetrahedral structure (I). For a molecule of this symmetry

(C_{3v}), four ($2a_1 + 2e$) terminal and two ($a_1 + e$) bridging carbonyl stretching absorptions are allowed by group theory; four terminal and one bridging carbonyl bands are observed.



It is of interest to note the relationship of this structure to other tetranuclear clusters containing cobalt atoms, *e.g.* $Co_4(CO)_{12}$ [structure(II)]^{9,10} and $HMCo_3(CO)_{12}$ ($M = Fe^{11,12}$, Ru^{12} and Os^{13}), which also contain bridging carbonyl groups. The stretching frequencies of the bridging carbonyls in $\pi-C_5H_5NiCo_3(CO)_9$ and $Co_4(CO)_{12}$ are similar (1850 and 1867 cm^{-1} respectively). Although possessing a similar metal-atom framework, complexes of the type $RECo_3(CO)_9$ ($E = C, Si, Ge$ -or Sn ; $R = Cl, Br, I, \text{alkyl or aryl}$)¹⁴ have no bridging carbonyl groups.

Reaction of $[\pi-C_5H_5Ni(CO)]_2$ with $Fe_2(CO)_9$

The green crystalline, diamagnetic complex $(\pi-C_5H_5)_2Ni_2Fe(CO)_5$ was isolated from the reaction of $[\pi-C_5H_5Ni(CO)]_2$ with $Fe_2(CO)_9$ in light petroleum and was identified by analysis and mass spectroscopy. It is reasonably air-stable in the solid state but solutions in organic solvents deteriorate slowly.

Its NMR spectrum exhibits a singlet resonance due to the cyclopentadienyl protons and the chemical shift value is close to that of $[\pi-C_5H_5Ni(CO)]_2$, indicating that the cyclopentadienyl groups are still bonded to the nickel atoms.

The molecular ion, $(C_5H_5)_2Ni_2Fe(CO)_5^+$ and fragment multiplets attributable to the ions $(C_5H_5)_2Ni_2Fe(CO)_n^+$ ($n = 0-4$) are observed in the mass spectrum. An interesting feature of the spectrum is the competitive loss of iron and nickel atoms leading to the formation of the series of ions $(C_5H_5)_2NiFe(CO)_n^+$ ($n = 0-3$) and $(C_5H_5)_2Ni_2(CO)_n^+$ ($n = 0-2$).

The IR spectrum of $(\pi-C_5H_5)_2Ni_2Fe(CO)_5$ in the carbonyl region shows absorptions due to terminal and bridging carbonyl groups. For trinuclear and higher clusters, since there are two possible sites for bridging carbonyl groups—in edge- and face-bridging positions—some additional information is required to assign a structure to the molecule. This is provided by determining the ranges of frequency to be expected for stretching vibrations of both doubly and triply bridging carbonyl groups in related molecules whose structures in the solid state can be or have been unequivocally determined. Existing data for neutral complexes of this type (Table 2) shows that the frequency ranges to be expected for vibrations of edge- and face-bridging carbonyl groups are $1810-1860$ and $1720-1740\text{ cm}^{-1}$ respectively.

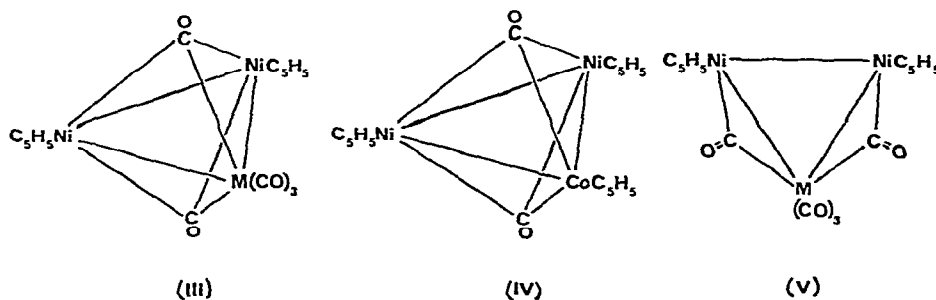
In a nujol mull, the IR spectrum of the complex shows two bridging carbonyl absorptions at 1730 and 1777 cm^{-1} . Using the available data (Table 2), the absorption

TABLE 2
 INFRARED SPECTRA

Complex	Phase	$\nu(\text{C-O})^a$	Ref.
$\pi\text{-C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9$	n-Hexane	2082 s 2043 vs 2025 s 2013 m 1850 s	b
$(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$	Nujol mull	2040 s 1980 s(br) 1942 s(sh) 1777 w(sh) 1730 m	b
	n-Hexane	2050 vs 2004 s 1983 s 1823 vw 1790 w 1762 m	b
	THF	2044 vs 1991 s 1975 s(sh) 1814 w(sh) 1774 m(sh) 1746 m	b
$[\text{Me}_2\text{N}][(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]$	Nujol mull	1964 s 1890 s 1853 s 1738 m 1671 m	b
	THF	1971 vs 1896 s 1878 s(sh) 1744 w 1688 m 1647 w(sh)	b
$[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$	Nujol mull	1855 s 1811 vs	b
$(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$	Nujol mull	1733	b
	THF	1775 w 1748 s	b
$(\pi\text{-C}_5\text{H}_5)_2\text{NiFe}(\text{CO})_3$		1975 1836(sh) 1806	4
$(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3\text{Co}(\text{CO})_2$		1723	6,7
$(\pi\text{-C}_5\text{H}_5)_3\text{Co}_3(\text{CO})\text{O}$		1720	7

^a In cm^{-1} ; s = strong, m = medium, w = weak, v = very, (sh) = shoulder and (br) = broad. ^b This work.

at 1730 cm^{-1} may be attributed to a face-bridging carbonyl group and since the other band could be due to a carbonyl group of this type, we suggest that the most probable structure for $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ in the solid state is (III) ($\text{M} = \text{Fe}$). This may be regarded as derived from that of $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_2\text{Co}(\text{CO})_2$ [(structure(IV)]^{6,7} by replacement of the $\pi\text{-C}_5\text{H}_5\text{Co}$ group by $\text{Fe}(\text{CO})_3$. Another related molecule is the acetylene complex, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{PhC}_2\text{Ph})\text{Fe}(\text{CO})_3$ ⁴, which has the same metal atom framework.



Evidence concerning the structure of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ in solution is even more difficult to obtain, but some attempt has been made by comparing the solution IR spectrum of the complex with those of other related species such as $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ and $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ in the same solvent. We have found that the IR spectrum of $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ in tetrahydrofuran (THF) contains two bridging carbonyl bands, and this is unexpected if the D_{3h} structure of this molecule in the solid state¹⁵ is retained in solution. Two possible explanations for this observation are that more than one species is present in solution or that there exists a single species having symmetry lower than D_{3h} . Although the relative intensity of the two absorptions does not vary with temperature, it does change with different solvents. Thus, neither of the two possibilities can be ruled out on this basis.

In solution, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ shows a total of six carbonyl stretching

TABLE 3

MONOISOTOPIC MASS SPECTRUM OF $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5^+$

Ion	<i>m/e</i>	Relative intensity
$(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5^+$	442	1.5
$(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_4^+$	414	1.6
$(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_3^+$	386	2.0
$(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_2^+$	358	2.3
$(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})^+$	330	7.7
$(\text{C}_5\text{H}_5)_2\text{NiFe}(\text{CO})_3^+$	328	5.1
$(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}^+$	302	30.6
$(\text{C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2^+$		
$(\text{C}_5\text{H}_5)_2\text{NiFe}(\text{CO})_2^+$	300	8.7
$(\text{C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})^+$	274	1.2
$(\text{C}_5\text{H}_5)_2\text{NiFe}(\text{CO})^+$	272	8.6
$(\text{C}_5\text{H}_5)_2\text{Ni}_2^+$	246	14.2
$(\text{C}_5\text{H}_5)_2\text{NiFe}^+$	244	16.2
$(\text{C}_5\text{H}_5)_2\text{Ni}^+$	188	44.8
$(\text{C}_5\text{H}_5)_2\text{Fe}^+$	186	100
$(\text{C}_5\text{H}_5)\text{Ni}^+$	123	35.3
$(\text{C}_5\text{H}_5)\text{Fe}^+$	121	33.3

^a Taken at a source temperature of 70° and source pressure of 2×10^{-7} mm. The characteristic isotope pattern was observed for each ion.

absorptions, three in the terminal region and three in the bridging region. Since group theory predicts that no more than five absorptions are allowed for any one species in solution but that five are expected for possible structures such as (III) and (V), a possible explanation for this observation is that isomerism between two of these structural forms exists. If we assume that at least one of the carbonyl bands in the solution spectrum of $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ is due to a face-bridging carbonyl group, then because of the similar frequencies, it follows that one of the forms of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{-Fe}(\text{CO})_5$ in solution is also likely to possess triply bridging carbonyl groups.

Although more than one isomeric form of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ may be present in solution, the Mössbauer spectrum of the crystalline solid obtained shows a single sharp quadrupole-split doublet, indicating that only one form is present.

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Mn}(\text{CO})_5^-$

The reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Mn}(\text{CO})_5^-$ in refluxing THF during half an hour gives the anion $[(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]^-$ which was isolated as its tetramethylammonium salt. This green diamagnetic compound, which is isoelectronic with $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$, was characterised by analysis. It is extremely air-sensitive both in the solid state and in solution.

The NMR spectrum of $[\text{Me}_4\text{N}][(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]$ shows two singlets whose intensity ratio is 5/6, and these may be attributed to the cyclopentadienyl and methyl protons respectively. Again, the chemical shift value of the cyclopentadienyl resonance indicates that these groups remain attached to the nickel atoms.

The IR spectrum of the complex in the solid state is similar to that of $(\pi\text{-C}_5\text{H}_5)_2\text{-Ni}_2\text{Fe}(\text{CO})_5$ but the absorptions are shifted to lower frequency because of the negative charge. Allowing for this frequency shift, the absorption at 1671 cm^{-1} in the solid state spectrum of $[\text{Me}_4\text{N}][(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]$ may be attributed to a

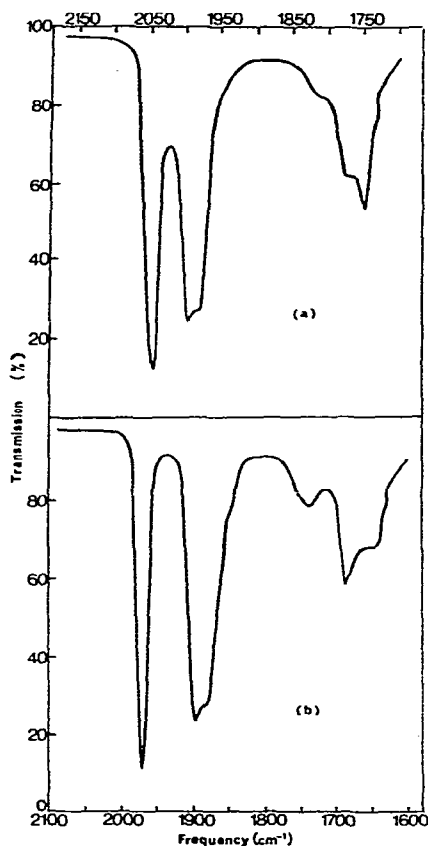


Fig. 1. The IR spectra of (a) $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ and (b) $[\text{Me}_3\text{N}][(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]$, in tetrahydrofuran.

face-bridging carbonyl group. In this case, the anion $[(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]^-$ would be isostructural with $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ as in structure (III). We believe that this would be the first molecule in which a manganese atom is bonded to a bridging carbonyl group.

The solution IR spectrum of the anion $[(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]^-$ bears a close resemblance to that of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ and likewise, shows a total of six carbonyl absorptions (Fig. 1). Hence, it appears that isomers are present as in the case of the nickel-iron complex.

Reactions of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with other metal carbonyl species

The reactions of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Ru}_3(\text{CO})_{12}$ and with the tetrahydrofuran adduct, $\text{Mo}(\text{CO})_5\text{THF}$, have been investigated. From the reaction mixture, the known complexes $[\pi\text{-C}_5\text{H}_5\text{Ru}(\text{CO})_2]_2$ and $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ were respectively identified.

EXPERIMENTAL

General

All manipulations were performed under nitrogen. Solvents employed were

AnalaR grade and were degassed before use.

IR spectra of the complexes in the carbonyl region ($2150\text{--}1600\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 257 grating instrument and were calibrated against carbon monoxide. NMR spectra in acetone- d_6 were run on either a Perkin-Elmer R10 or a Varian Associates HA 100 spectrometer operating at 60 and 100 MHz respectively, using TMS as an internal reference. Mass spectra were obtained on an A.E.I. MS9 mass spectrometer with an ionising energy of 70 eV and an ionising current of 100 μA . The starting materials were prepared according to standard literature methods.

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Co}_2(\text{CO})_8$

A mixture of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ (0.5 g, 1.65 mmole) and $\text{Co}_2(\text{CO})_8$ (0.5 g, 1.46 mmole) in 50 ml of light petroleum (b.p. $60\text{--}80^\circ$) was gradually warmed to its boiling point. After refluxing for 2–3 min, the resulting deep green solution was cooled to room temperature. Thin layer chromatographic (TLC) analysis showed, besides the starting materials, the presence of $\text{Co}_4(\text{CO})_{12}$ (identified by IR spectroscopy) together with a green compound. After centrifuging, the solution was chromatographed on a column of silica gel. The unreacted $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ (red band) together with $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ (dark brown bands) were removed by first eluting with light petroleum (b.p. $40\text{--}60^\circ$). Further elution with 1/5 benzene/light petroleum gave a deep green solution. Removal of the solvent *in vacuo* followed by recrystallisation from a small volume of light petroleum (b.p. $30\text{--}40^\circ$) afforded deep green to almost black crystals of $\pi\text{-C}_5\text{H}_5\text{NiCo}_3(\text{CO})_9$ (yield 20%). (Found: C, 30.41; H, 1.05. $\text{C}_{14}\text{H}_5\text{Co}_3\text{NiO}_9$ calcd.: C, 30.42; H, 0.91%). The ^1H NMR spectrum exhibited a singlet at τ 4.90 ppm.

Subsequent elution with CH_2Cl_2 gave $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ identified by IR spectroscopy.

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Fe}_2(\text{CO})_9$

A mixture of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ (0.5 g, 1.65 mmole) and $\text{Fe}_2(\text{CO})_9$ (1.0 g, 2.75 mmole) in 30 ml of light petroleum (b.p. $60\text{--}80^\circ$) was gradually warmed to its boiling point during 10 min. The resulting greenish brown solution was cooled to room temperature. TLC analysis showed that all the $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ had reacted and that no $\text{Fe}_3(\text{CO})_{12}$ had formed. The solution was then centrifuged and cooled to -78° ; the black solid deposited was recrystallised several times from light petroleum (b.p. $30\text{--}40^\circ$) to give large dark green to black crystals of $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ (yield 82%). (Found: C, 40.45; H, 2.35. $\text{C}_{15}\text{H}_{10}\text{FeNi}_2\text{O}_5$ calcd.: C, 40.63; H, 2.27%). The ^1H NMR spectrum showed a singlet at τ 4.60 ppm. The Mössbauer spectrum (recorded at 80° K) exhibited a doublet with $\delta = 0.30 \pm 0.02$ mm/sec (relative to sodium nitroprusside), $\Delta = 1.10 \pm 0.02$ mm/sec and $\Gamma = 0.34$ mm/sec.

Prolonged refluxing of the mixture gave mainly $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, identified by TLC and IR spectroscopy.

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Mn}(\text{CO})_5^-$

A solution of $\text{NaMn}(\text{CO})_5$, prepared by sodium amalgam reduction of $\text{Mn}_2(\text{CO})_{10}$ (0.5 g, 1.28 mmole) in 7 ml of anhydrous THF, was added to solid $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ (0.5 g, 1.65 mmole). After refluxing for 30–35 min, the deep brown reaction

mixture was cooled and the solvent removed *in vacuo*. The black residue was extracted twice (35–45 ml each) with light petroleum (b.p. 30–40°) to remove unreacted $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ and $\text{Mn}_2(\text{CO})_{10}$, followed by extraction with 40 ml of water. The deep green solution was treated with an aqueous solution of Me_4NCl , producing a deep green precipitate. Recrystallisation of the product from methanol gave large black crystals of $[\text{Me}_4\text{N}][(\pi\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{Mn}(\text{CO})_5]$ (yield 65%). (Found: C, 44.7; H, 4.4; N, 2.4. $\text{C}_{19}\text{H}_{22}\text{MnNNi}_2\text{O}_5$ calcd.: C, 44.2; H, 4.3; N, 2.7%.) The ^1H NMR spectrum showed two singlets at τ 4.98 ($\pi\text{-C}_5\text{H}_5$) and τ 6.52 (CH_3) ppm.

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Ru}_3(\text{CO})_{12}$

On warming a mixture of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ (0.5 g, 1.65 mmole) and $\text{Ru}_3(\text{CO})_{12}$ (0.5 g, 0.78 mmole) in 50 ml of light petroleum (b.p. 80–100°) for 10 min, the starting materials were recovered together with some $[\pi\text{-C}_5\text{H}_5\text{Ru}(\text{CO})_2]_2$ (identified by its IR and mass spectra) and $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ (identified by TLC and IR spectra).

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ with $\text{Mo}(\text{CO})_5\text{THF}$

A solution of $\text{Mo}(\text{CO})_5\text{THF}$, prepared by UV irradiation of a solution of $\text{Mo}(\text{CO})_6$ (0.5 g, 1.89 mmole) in 60 ml of refluxing THF¹⁶, was added to a solution of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ (0.5 g, 1.65 mmole) in 10 ml of THF. The mixture was gently refluxed and the reaction was monitored by TLC. After 7 h, TLC analysis indicated the presence of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{CO})]_2$ (confirmed by its IR spectrum) together with $\text{Mo}(\text{CO})_6$, $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ and $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}_3(\text{CO})_2$ (all identified by IR spectra).

ACKNOWLEDGEMENTS

We thank Dr. M. J. Mays for helpful discussions, Mr. E. T. Libbey for assistance in obtaining the Mössbauer spectrum, the British Council for an award (to A.T.T.H.) and the S.R.C. for a maintenance grant (to J.K.).

REFERENCES

- 1 W. HIEBER AND J. ELLERMANN, *Z. Naturforsch. B*, 18 (1963) 589, 595 and references therein.
- 2 E. O. FISCHER AND C. PALM, *CChem. Ber.*, 91 (1958) 1725.
- 3 J. F. TILNEY-BASSETT, *Proc. Chem. Soc.*, (1960) 419.
- 4 J. F. TILNEY-BASSETT, *J. Chem. Soc.*, (1963) 4784.
- 5 K. YASUFUKU AND H. YAMAZAKI, *Bull. Chem. Soc. Jap.*, 42 (1969) 3049; 43 (1970) 1588.
- 6 L. F. DAHL, in M. CAIS (Ed.), *Progress in Coordination Chemistry*, Elsevier, Amsterdam, 1968, p. 244; V. A. UCHTMAN AND L. F. DAHL, submitted for publication (cited in ref. 7).
- 7 V. A. UCHTMAN AND L. F. DAHL, *J. Amer. Chem. Soc.*, 91 (1969) 3763.
- 8 P. CHINI, S. MARTINENGO AND V. ALBANO, *Proc Symp. Metal Carbonyls, Venice*, 1968, A3.
- 9 C. H. WEI AND L. F. DAHL, *J. Amer. Chem. Soc.*, 88 (1966) 1821.
- 10 C. H. WEI, *Inorg. Chem.*, 8 (1969) 2384.
- 11 P. CHINI, L. COLLI AND M. PERALDO, *Gazz. Chim. Ital.*, 88 (1960) 1005.
- 12 M. J. MAYS AND R. N. F. SIMPSON, *J. Chem. Soc. A*, (1968) 1444.
- 13 J. KNIGHT AND M. J. MAYS, *J. Chem. Soc. A*, (1970) 711.
- 14 J. F. YOUNG, *Advan. Inorg. Chem. Radiochem.*, 11 (1968) 92.
- 15 A. A. HOCK AND O. S. MILLS, in S. KIRSCHNER (Ed.), *Advances in the Chemistry of the Coordination Compounds*, MacMillan, New York, 1961, p. 640.
- 16 W. STROHMEIER, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 730.