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Tautomerism in some [η-dienyl)FeCo(CO)$_5$(L)] Complexes (dienyl = C_5H_5, MeC_5H_4 or C_9H_7; L = tertiary phosphine, phosphite or arsine)

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*Various new [(η-dienyl)FeCo(CO)$_5$(L)] derivatives are reported (dienyl = C_5H_5, MeC_5H_4 or C_9H_7; L = tertiary phosphine, or arsine). Some are found as CO-bridged (μ) species in the solid state, others as non-bridged (*nb*) isomers. In solution, many exist as equilibrium mixtures of one* nb *and at least two, and perhaps four, μ tautomers. The* nb *isomers are favoured by higher temperatures, bulky ligands, and along the series dienyl = $C_9H_7 \gg MeC_5H_4 > C_5H_5$. The solvent has little effect on the μ-*nb *equilibria.*

Introduction

The equilibrium between the CO-bridged (μ) and non-bridged (*nb*) isomers in solutions of [$Co_2(CO)_8$] [1–3] is profoundly modified when two CO ligands are replaced by monodentate tertiary phosphines, arsines or stibines (L) [4].

Here, we report studies of the consequences of similar substitution on the tautomeric equilibria observed [5] in solutions for solutions of the [(η-dienyl)FeCo(CO)$_6$] derivatives (dienyl = C_5H_5, MeC_5H_4, or C_9H_7).

Experimental

Chemicals were purchased from the usual sources. Previously reported methods were used to prepare the [$Co_2(CO)_6(L)_2$] [4], [(η-C_5H_5)Fe(CO)$_2$Cl] [6], [(η-MeC_5H_4)Fe(CO)$_2$Cl [7], [(η-C_9H_7)Fe(CO)$_2$I] [8], and [(η-dienyl)FeCo(CO)$_6$] complexes (dienyl = C_5H_5, MeC_5H_4 and C_9H_7 [5]. All reactions were carried out at room temperature, under an atmosphere of nitrogen, and in purified solvents.

Most [(η-dienyl)FeCo(CO)$_5$(L)] derivatives were prepared by the addition of [(η-dienyl)Fe(CO)$_2$X] (X = Cl or I) to a tetrahydrofuran solution (50 ml) of Na[Co(CO)$_3$(L)] (mol ratio 1.2:1) prepared *in situ* by the reduction of [($Co_2(CO)_6(L)_2$] (*ca.* 1.5 g) with cleaned sodium wire. The products were isolated by removal of the solvent at reduced pressure, separated by chromatography (benzene/petrol and alumina), and purified by crystallization from pentane or toluene/pentane mixtures. Yields were 2–35%.

The reaction of [(η-C_5H_5)FeCo(CO)$_6$] (1 g) with P(OPh)$_3$ (*ca.* 1 ml) in tetrahydrofuran gave [(η-C_5H_5)-FeCo(CO)$_5${P(OPh)$_3$}]. Other ligands gave only [(η-dienyl)Fe(CO)$_2$(L)] [Co(CO)$_4$] salts.†

Melting points and analyses† for the [(η-dienyl)-FeCo(CO)$_5$(L)] compounds are recorded in Table I. Iron was estimated as described [9].

I.r. spectra were obtained as reported previously [4]. They are summarised in Tables II and III.

Results

The [(η-dienyl)Fe(CO)$_2$(L)] [Co(CO)$_4$] salts are air-stable brown solids which oxidise rapidly in solution. The i.r. spectra are similar; that of [(η-C_5H_5)-Fe(CO)$_2$(PPh$_3$)] [Co(CO)$_4$] shows two absorption bands at 2014 and 2056 cm^{-1} due to the C–O stretching ν(CO) vibrations of the cation, and another at 1890 cm^{-1} due to the anion.

The dark brown [(η-dienyl)FeCo(CO)$_5$(L)] complexes are slowly oxidised in air. They disproportionate to [(η-dienyl)$_2$Fe$_2$(CO)$_4$] and [$Co_2(CO)_6(L)_2$]. Although this is always rapid above 35 °C, it is most marked for the (η-C_9H_7) derivatives, and is complete within 24 hr for solid [(η-C_9H_7)FeCo(CO)$_5${P(Bu^n)$_3$}] at –20 °C.

The i.r. spectra of the [(η-dienyl)FeCo(CO)$_5$(L)] derivatives show that they exist as either C–O bridged (μ) or non-bridged (*nb*) isomers in the solid state (Table II). However, their solutions in organic solvents often contain more than one species. Unfortunately identification and assignment of absorption bands A–K was often difficult. Many have irregular profiles with ill-defined shoulders, which are not included in the Table II, and probably contain more than one component, *e.g.* in solutions of [(η-C_9H_7)FeCo(CO)$_5$-(PPhMe$_2$)] G is a resolved doublet (Table II). Further-

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† [(η-C_5H_5)Fe(CO)$_2$(PPh$_3$)] [Co(CO)$_4$] was recrystallized from CH_2Cl_2 in 95% yield. *Anal.* Found %C = 56.3, %H = 3.5; required %C = 57.0 and %H = 3.3.

TABLE I. Melting Points and Analyses for Some [(η-dienyl)FeCo(CO)$_5$(L)] Compounds.

Dienyl	L	M.p. (°C)[a]	Found %			Required (%)		
			C	H	Fe	C	H	Fe
C_5H_5	$PPh(^iPr)_2$	102 - 104 (d)	50.8	4.9	10.8	51.4	4.7	10.9
	$P(^nPr)_3$	86 - 87 (d)	47.7	5.6	11.9	47.5	5.4	11.7
	$As(^nPr)_3$	76 - 77 (d)	42.8	5.1	10.6	43.5	5.0	10.7
	$As(^iPr)_3$	dec. 68	43.8	4.9	10.4	43.5	5.0	10.7
	$PPh(^nBu)_2$	62 - 64 (d)	53.4	5.4	10.6	53.2	5.2	10.3
	$PPh_2(^nBu)$	90 - 92 (d)	55.1	4.3	10.3	55.3	4.3	10.0
	PPh_3	174 - 176 (d)	57.9	3.5	10.0	57.7	3.4	9.6
MeC_5H_4	$PPh_2(^nBu)$	70 - 71 (d)	55.8	4.8	9.8	56.2	4.5	9.8
	PPh_3	dec. 235	57.9	3.4	9.5	58.4	3.7	9.4
C_9H_7	$PPh(Me)_2$	178 - 180	51.5	3.6	11.2	51.9	3.7	11.0
	$PPh(^nBu)_2$	60 (d)	56.7	5.0	10.0	56.7	5.1	9.5
	$PPh_2(^nBu)$	dec. 60	58.8	4.4	9.3	58.8	4.2	9.2
	$PPh_3 \cdot 2/3C_7H_8$[b]	238 (d)	63.2	3.8		63.5	3.9	

[a] Measured in sealed tubes. (d) = melts with decomposition. dec. = decomposes without melting. [b] N.m.r. spectra indicate 2/3 mol of toluene of solvation per mol of complex.

more changes in peak shapes for A–D (Table III) imply that more than four absorption bands are present but irresolvable.

The intensities of the absorption bands due to the *nb* species relative to those due to the μ forms[≠] (as measured by the intensity ratio K:J or K:A + B) increase along the series dienyl = $C_9H_7 \ll MeC_5H_4 < C_5H_5$, and L = $^nPr_3As < {^iPr_3As}$; $PhMe_2P < Ph^nBu_2P$; $^nPr_3As < {^nPr_3P}$; and $Ph_2{^nBuP} < Ph^nBu_2P$; $^nBu_3P < Ph_3P$. They are favoured by higher temperatures, but changes in the solvent have little effect. The relative intensities of absorption bands A–D vary non-systematically with the above four variables.

Attempts to obtain p.m.r. spectra of the [(η-dienyl)FeCo(CO)$_5$(L)] derivatives at various temperatures failed. The compounds disproportionated too quickly.

Discussion

Tertiary phosphines displace the [Co(CO)$_4$]$^-$ ion from [(η-dienyl)FeCo(CO)$_6$], with Ph_3As the reaction is incomplete in tetrahydrofuran, and Ph_3Sb fails to react. The i.r. spectra of the [(η-dienyl)Fe(CO)$_2$(L)]$^+$[Co(CO)$_4$]$^-$ are consistent with the presence of these cations [10] and anions [11].

On the other hand, triphenylphosphite gives [(η-C_5H_5)FeCo(CO)$_5${P(OPh)$_3$}] in this reaction. It may be formed *via* a labile intermediate salt (*cf.* $Co_2(CO)_8$ and Ph_3P [12, 13].

The most convenient route to the [(η-dienyl)FeCo(CO)$_5$(L)] complexes was the reaction of [(η-dienyl)Fe(CO)$_2$X] with Na[(Co(CO)$_3$L] (X = Cl or I). It is limited as the expected sodio-derivative is not always obtained by the reduction of [$Co_2(CO)_6(L)_2$] [14], whilst sodium wire had to be used in place of its amalgam as the presence of [Hg{Co(CO)$_3$(L)}$_2$] made product purification difficult.

The [*nb*-(η-dienyl)FeCo(CO)$_5$L] species have similar i.r. spectra (Table II), and probably have the structure shown in Fig. 1. All known [RCo(CO)$_3$(L)] complexes have trigonal bipyramidal coordination about Co with the phosphine ligand L and the group R mutually *trans* and occupying the two axial coordination positions (*e.g.* [*trans*-$CHF_2CF_2Co(CO)_3(PPh_3)$] [15]. The pseudo-octahedral piano-stool ligand distribution is the only one observed for [(η-dienyl)Fe(CO)$_2$X] complexes (*e.g.* [(η-C_5H_5)Fe(CO)$_2$ SnCl$_3$][16]. Only *nb* isomers are found in the solutions of some complexes, but for other CO-bridged forms are present and may predominate (Tables II and III).

Structures have been postulated for the two [(η-dienyl)Fe(CO$_\mu$)$_2$Co(CO)$_4$] tautomers [5]. One is adopted by both [(η-C_9H_7)FeCo(CO)$_6$ [17] and [(η-C_5H_5)FeCo(CO)$_6$] [18] in the solid state, but they differ slightly in ligand distribution about the Co atom. From this may be derived two possible isomers of [μ-(η-dienyl)FeCo(CO)$_5$(L)], (I) and (II) in Fig. 1 of which the overall geometry depicted in the first is that adopted by [μ-(η-C_5H_5)FeCo(CO)$_5$(PPh$_2$Me)] in the solid state [19]. The second postulate gives rise to (III) and (IV). It is assumed that the ligand L remains coordinated to the cobalt atom. Each isomer should give rise ro two absorption bands due to its ν(CO$_\mu$) vibrations. The presence of four well-defined such peaks or shoulders, A–D, in their i.r. spectra point to at least two μ-isomers being present. In certain instances *e.g.* solutions of [(η-C_9H_7)FeCo(CO)$_5$(L)] (L = $Ph_2{^nBuP}$ and $PhMe_2P$) at low temperatures, one μ species predominates. The relative intensities of its ν(CO$_\mu$) absorption bands are consistent with the geometry of the Fe(CO$_\mu$)$_2$CO bridging system, and

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[≠] The division of absorption bands is summarised in Table II.

TABLE II. The I.r. Spectra (1700–2100 cm^{-1}) of $[(\eta\text{-dienyl})FeCo(CO)_5(L)]$ Complexes in Hexane Solution at 25 °C (peak positions (cm^{-1}) with relative heights in parentheses).

L	Absorption Bands										
	A	B	C	D	E	F	G	H	I	J	K
dienyl = C_5H_5											
$PPh(^iPr)_2$[b]					1911(2.6)	1934(4.6)	1962(10)	1966(sh)			2025(7.0)
$P(^nPr)_3$	1777(0.14)	1793(0.21)	1825(sh)	1833(0.05)	1913(2.5)	1935(4.7)	1959(10)	1965(sh)	1980(sh)	2015(sh)	2022(7.9)
$As(^nPr)_3$	1778(0.8)	1787(sh)	1825(0.2)	1831(sh)	1913(2.8)	1934(5.0)	1960(10)	1967(sh)	1981(2.6)	2016(sh)	2024(8.0)
$As(^iPr)_3$	1786(0.07)	1793(sh)		1828(0.02)	1908(2.9)	1930(4.8)	1958(10)	1966(sh)	1978(sh)		2022(7.9)
$PPh(^nBu)_2$	1782(0.16)	1791(sh)		1828(0.03)	1912(1.5)	1936(3.3)	1958(10)	1965(sh)	1982(sh)	2017(sh)	2024(4.2)
$PPh(^nBu)$	1784(0.4)	1796(sh)	1826(sh)	1831(0.1)	1914(1.6)	1940(3.9)	1961(10)	1968(sh)	1985(1.8)	2019(2.0)	2025(5.2)
PPh_3[b]	1790(0.1)				1920(2.5)	1943(4.8)	1962(10)	1971(3.8)	1982(sh)	2021(sh)	2026(6.5)
$P(OPh)_3$[b]	1802(0.1)				1932(1.4)	1960(sh)	1969(10)	1980(3.4)		2036(sh)	2040(5.6)
dienyl = MeC_5H_4											
$PPh_2(^nBu)$	1782(0.7)	1794(sh)		1828(0.1)	1913(1.2)	1940(sh)	1955(10)	1966(sh)	1981(2.3)	2015(2.5)	2022(4.0)
PPh_3	1785(0.1)				1918(2.7)	1939(5.9)	1957(10)		1978(3.9)	2019(sh)	2025(6.9)
dienyl = C_9H_7											
$P(^nBu)_3$	1776(0.7)	1789(1.2)	1825(0.2.br)		1913(2.2)	1937(5.2)	1955(10)	1966(4.8)	1975(5.2)	2011(6.0)	2020(6.0)
$PPhMe_2$	1781(2.7)	1793(5.1)	1825(sh)	1832(1.3)	1919(1.4)	1945(sh)	1956(10)	1962(10)	1980(11.0)	2014(11.2)	2022(sh)
$PPh(^nBu)_2$	1781(1.0)	1795(2.3)	1821(sh)	1826(0.5)	1916(1.5)	1941(sh)	1958(10)	1969(4.4)	1980(7.0)	2014(8.3)	2029(4.9)
$PPh_2(^nBu)$	1781(1.7)	1794(2.5)	1823(sh)	1831(0.7)	1917(1.2)	1941(sh)	1957(10)	1970(3.5)	1981(8.2)	2014(9.0)	2023(3.5)
PPh_3[c]	1788(sh)	1795(1.0)	1822(0.2)		1916(1.9)	1940(sh)	1958(10)	1968(4.2)	1978(sh)	2011(3.6)	2021(5.4)

[a] Due solely or in part to *nb* isomers. The remainder are due solely to the b tautomers. [b] Found as *nb* species in the solid state. [c] CS_2 solution.

TABLE III. The Effects of Solvent and Temperature on the I.r. Spectra (1700–2100 cm^{-1}) of Some [(η-dienyl)FeCo(CO)$_5$(L)] derivatives.

Solvent[b]	Absorption Bands[a]										
	A	B	C	D	E	F	G	H	I	J	K
[(η-C$_9$H$_7$)FeCo(CO)$_5$(PMe$_2$Ph)]											
CS$_2$	1775(sh)	1785(4.5)	1813(sh)	1819(1.2)	1911(sh)		1944(10)		1973(9.6)	2008(10.9)	2015(sh)
CS$_2$ (−80 °C)	1780(8.3)	1788(sh)	1813(1.7)	1819(sh)			1942(10)		1971(9.6)	2007(12.2)	
THF	1781(sh)	1789(5.4)		1817(1.3.br)	1915(sh)		1944(10)		1969(10.2)	2007(9.5)	2014(sh)
MeCN	1771(sh)	1778(7.0)	1791(sh)				1943(10)		1963(13.5)	2008(11.5)	
Nujol mull	1775(s)	1786(sh)				1933(s)	1951(m)	1960(m)		2007(s)	
[(η-C$_9$H$_7$)FeCo(CO)$_5$(PPh$_2$^{n}Bu)]											
25% CS$_2$/ 75% Hexane	1780(1.9)	1792(2.4)	1822(0.5)	1831(sh)	1917(sh)	1942(sh)	1954(10)	1970(sh)	1977(6.5)	2012(8.4)	2020(4.0)
25% CS$_2$/ 75% Hexane (−80 °C)	1779(5.6)	1793(5.2.sh)	1822(1.1)	1830(sh)		1940(sh)	1950(10)	1970(sh)	1976(9.6)	2011(11.5)	
CS$_2$	1780(sh)	1790(2.0)	1823(0.5.br)		1907(sh)	1938(sh)	1949(10)		1975(5.7)	2010(7.0)	2018(3.6)
THF	1781(sh)	1790(2.6)	1815(0.6)	1824(sh)	1915(sh)	1933(sh)	1947(10)		1970(6.9)	2007(6.6)	2015(3.5)
MeCN	1782(3.0.br)		1804(sh)				1944(10)		1969(7.7)	2003(7.3)	2013(sh)
Nujol mull	1776(s)		1820(m)				1934(vs)		1956(vs)	2000(s)	

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses measured at 25 °C unless stated otherwise. m = medium, s = strong, vs = very strong, sh = shoulder, and br = broad.

[b] THF = tetrahydrofuran.

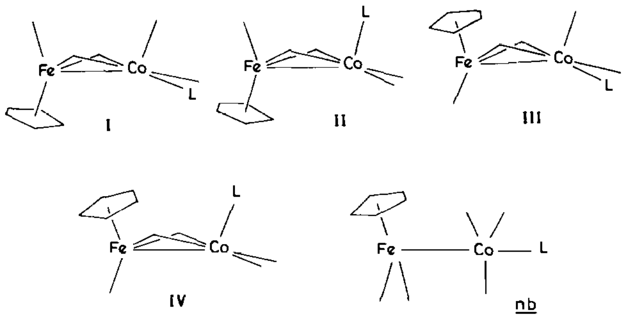

Figure 1. Proposed structures for the *nb* and four b isomers of the [(η-dienyl)FeCo(CO)$_5$(L)] complexes. CO ligands have been omitted for the sake of clarity.

presumably of the whole molecule, not changing markedly on replacement of a CO ligand by a phosphine or arsine (*cf.* the structures of [(η-C_5H_5)FeCo(CO)$_5$-L)] (L = CO [18] or Ph_2MeP [19] in the solid state.

Although various factors affect the equilibria between the μ-isomers, they are not amenable to analysis. On the other hand variations in μ-*nb* equilibria may be rationalized in the same way as have those for [$Co_2(CO)_6(L)_2$] systems using similar assumptions [4]. Of particular interest are the consequences of changing L. Decreasing the electron-donating effects of L either by going from R_3P to R_3As or by variations in R tend to destabilize the equilibria towards the μ-species. Increasing the bulk of L has the opposite effect due to increased interligand interactions across the Co–Fe bond in the μ-isomers which are not affected in the *nb*-forms. Sometimes these effects act in opposition as in the series L = $^{n}Bu_3P$, $Ph^{n}Bu_2$, $Ph_2{}^{n}BuP$ and Ph_3P for dienyl = C_5H_5 or C_9H_7 where the abrupt decline in the μ/*nb* ratio for the Ph_3P complexes is probably a consequence of the steric effects of the ligand outweighing the electronic.

We are not able to account for the consequences of varying the (η-dienyl) ligand.

Lower temperatures favour the μ at the expense of the *nb* isomers, a common feature of tautomeric systems of this type (Table III) (*e.g.* ref. 4 and refs. therein).

The effects of changes in solvent are small (Table III). They lie between those observed for the [Co_2-$(CO)_6(L)_2$] [4] and [(η-C_5H_5)$_2M_2(CO)_4$] (M = Fe or Ru) [20] systems where more polar solvents favour the *nb* and μ isomers respectively [20].

The interconversion of the various isomers probably takes place by a mechanism similar to that proposed by Cotton *et al.* for other molecules (*e.g.* ref. 21). That is the opening of the Fe(CO$_\mu$)$_2$Co system to give (OC$_t$)Fe–Co(CO$_t$), and its subsequent reformation though not necessarily with the same carbonyl groups. Unfortunately the extreme instability of these [(η-dienyl)FeCo(CO)$_5$(L)] derivatives in solution has prevented us from investigating these processes by variable temperature n.m.r. spectroscopy.

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