# Preparation and Spectra of a Series of Tautomeric Compounds, [NiCo($\eta$-dienyl)(CO)$_4$L] (dienyl = $C_5H_5$ or $C_5H_4Me$; L = tertiary phosphine or arsine)

By **A. R. Manning**, Department of Chemistry, University College, Belfield, Dublin 4, Ireland

A number of [NiCo($\eta$-dienyl)(CO)$_4$L] complexes (dienyl = $C_5H_5$ or $C_5H_4Me$; L = tertiary phosphine or arsine) have been prepared from [Ni($\eta$-dienyl)LBr] and Na[Co(CO)$_4$] in tetrahydrofuran solution. During this reaction the ligand L migrates from Ni to Co. Infrared, $^1$H n.m.r., and mass spectroscopy have been used to investigate the structure of these compounds, which in solution exist as an equilibrium mixture of isomers. One has the [($\eta$-dienyl)(OC)NiCo(CO)$_3$L] structure with no bridging CO groups. The remainder contain the Ni($\mu$-CO)$_2$Co moiety, and structures are suggested for them. The equilibria are affected by changes of solvent, temperature, and the $\eta$-dienyl and L ligands. Variable-temperature $^1$H n.m.r. spectroscopic studies on [NiCo($\eta$-$C_5H_5$)(CO)$_4${P($C_6H_4F$-*p*)$_3$}] show that at room temperature the interconversion of isomers is slow on the n.m.r. time scale.

THE isoelectronic compounds [$Ni_2$($\eta$-$C_5H_5$)$_2$(CO)$_2$] [1] and [$Co_2$(CO)$_8$] [2] are familiar, but the mixed-metal complex [NiCo($\eta$-$C_5H_5$)(CO)$_5$] is unknown. Some of its [NiCo($\eta$-dienyl)(CO)$_4$L] derivatives (dienyl = $C_5H_5$ or $C_5H_4Me$; L = tertiary phosphine or arsine) are reported herein. They have been found to exist as mixtures of isomers in solution.

A preliminary account of this work has been published,[3] as have molecular-structure determinations by *X*-ray diffraction for three of the complexes [NiCo($\eta$-$C_5H_5$)(CO)$_4$L] where L = PEt$_3$[4] and P($C_6H_4F$-*p*)$_3$,[5] and [NiCo($\eta$-$C_5H_4Me$)(CO)$_4${P($C_6H_{11}$)Ph$_2$}].[6] More recently some very stable [NiCo($\eta$-$C_5H_5$)(RCCR)(CO)$_3$] derivatives have been prepared.[7]

## EXPERIMENTAL

Literature methods or adaptations of them were used to prepare many of the phosphines,[8] arsines,[8] and the [Ni($\eta$-dienyl)LBr] derivatives.[9] Other chemicals were purchased. All reactions were carried out at room temperature under an atmosphere of nitrogen in solvents which had been purified by refluxing over calcium hydride and distilling them prior to use.

Infrared spectra of some selected [NiCo($\eta$-$C_5H_5$)(CO)$_4$L] complexes in the 1 700—2 100 cm$^{-1}$ region at 25 °C unless stated otherwise

| L | Solvent [a] | Absorption bands [b] A | B | C | D | E | F | G | H | I |
|---|---|---|---|---|---|---|---|---|---|---|
| P($C_6H_{11}$)$_2$Ph [c] | Hexane | 1 813(sh)<br>1 817(10) | 1 827(4.4) | 1 849(4.6) | 1 911(0.5) | 1 943(0.7) | 1 974(7.0) | 1 981(19.4) | 2 024(7.9) | 2 029(16.2) |
| P($C_6H_{11}$)$_2$Ph [c] | Hexane (−78 °C) | 1 812(10)<br>1 817(sh) | 1 823(1.5) | 1 847(3.9) | | | 1 975(3.5, sh) | 1 981(17.0) | 2 024(sh) | 2 030(14.9) |
| PEt$_3$ | Hexane | 1 818(10) | 1 823(1.5) | 1 858(5.6) | 1 917(1.6) | 1 942(2.0) | | 1 979(13.7) | | 2 027(14.4) |
| PPh$_3$ | Hexane | 1 830(10) | 1 838(sh) | 1 861(5.0) | 1 925(4.3) | 1 946(4.5) | | 1 984(13.3) | | 2 029(16.0) |
| P($C_6H_4F$-*p*)$_3$ | Hexane | 1 831(10) | 1 841(sh) | 1 866(5.1) | 1 924(5.6) | 1 949(5.7) | | 1 988(15.6) | | 2 030(23.6) |
| P($C_6H_4F$-*p*)$_3$ | CS$_2$ | 1 825(10) | 1 831(sh) | 1 858(4.7) | 1 919(6.4) | 1 944(7.3) | | 1 980(16.7) | | 2 027(24.3) |
| P($C_6H_4F$-*p*)$_3$ | CS$_2$ (−78 °C) | 1 821(10) | | 1 853(4.1) | 1 917(0.9) | 1 945(1.1) | | 1 984(11.4) | | 2 028(10.2) |
| P($C_6H_4F$-*p*)$_3$ | Xylene | 1 826(10) | | 1 857(4.8) | 1 919(6.4) | 1 944(6.9) | | 1 980(15.6) | | 2 027(19.2) |
| P($C_6H_4F$-*p*)$_3$ | thf | 1 825(10) | | 1 854(4.5) | 1 918(4.9) | 1 942(5.5) | | 1 979(12.8) | | 2 026(14.7) |
| P($C_6H_4Cl$-*p*)$_3$ | Hexane | 1 831(10) | 1 841(sh) | 1 867(4.7) | 1 925(5.8) | 1 950(6.7) | | 1 986(15.5) | | 2 031(13.2) |
| P($C_6H_4Me$-*o*)Ph$_2$ | Hexane | 1 829(10) | 1 838(sh) | 1 860(4.8) | 1 926(2.1) | 1 952(2.4) | 1 979(sh) | 1 986(16.5) | | 2 032(15.6) |

[a] thf = Tetrahydrofuran. [b] Peak positions (cm$^{-1}$) with relative peak heights (optical densities) in parentheses. [c] With ($\eta$-$C_5H_5$) replaced by ($\eta$-$C_5H_4Me$).

The desired compounds were obtained by the addition of [Ni($\eta$-dienyl)LBr] (2.92 mmol) to a solution of Na[Co(CO)$_4$] in tetrahydrofuran (50 cm$^3$) prepared *in situ* by the reduction of [$Co_2$(CO)$_8$] (0.5 g, 1.46 mmol) with 1% sodium amalgam. The reaction mixtures were shaken for *ca.* 30 min, centrifuged, filtered, and the solvents removed at reduced pressure. The residues were purified by repeated recrystallizations from benzene–pentane, toluene–pentane, or ethanol–water mixtures to give the [NiCo($\eta$-dienyl)(CO)$_4$L] derivatives. As product purity was of greatest importance because of the complexity of the i.r. spectra, no attempt was made to maximise the reaction yields. Even so, these were generally 50—70%, but for L = AsMe$_3$ or AsPh$_3$ they were <1%.

The following complexes were obtained analytically pure. Their melting points (determined in sealed tubes) are given in parentheses: [NiCo($\eta$-$C_5H_5$)(CO)$_4$L] for L = PEt$_3$ (47—49), PBu$^n_3$ (30—32), P(CH$_2$Ph)$_3$ (104—105), PMe$_2$Ph (decomp. 70), PPr$^i_2$Ph (88—89), P($C_6H_{11}$)$_2$Ph (decomp. 108), P(CH$_2$Ph)Ph $_2$(100—102), PPh$_3$ (decomp. 180), P($C_6H_4Me$-*p*)$_3$ (141—143), P($C_6H_4Me$-*o*)Ph$_2$ (152—154), P($C_6H_4Me$-*o*)$_2$Ph (98—100), P($C_6H_4OMe$-*p*)$_3$ (decomp. 170), P($C_6H_4F$-*p*)$_3$ (158—160), P($C_6H_4Cl$-*p*)$_2$Ph (160—163), P($C_6H_4Cl$-*p*)$_3$ (162—163), AsMe$_3$ (decomp. 58), and AsPh$_3$·0.5$C_6H_6$ (78—80); and [NiCo($\eta$-$C_5H_4Me$)(CO)$_4$L] for L = P($C_6H_{11}$)$_2$Ph (100—102), P(CH$_2$Ph)$_2$Ph (124—126), P($C_6H_{11}$)Ph$_2$ (102—104), P(CH$_2$Ph)Ph$_2$ (91—93), PPh$_3$ (73—75), P($C_6H_4Me$-*p*)$_3$ (158—160), and P($C_6H_4OMe$-*p*)$_3$ (165—167 °C). Analyses were carried out in the Analytical Laboratory of University College Dublin.

Infrared spectra were obtained using a Perkin-Elmer 337 spectrometer fitted with a Hitachi–Perkin-Elmer readout recorder. They were calibrated with DCl and H$_2$O vapour [10] so that peak positions are generally accurate to ±1 cm$^{-1}$, but for shoulders the accuracy is much lower. Variable-temperature i.r. spectra were obtained using a VLT 2 (Research and Industrial Instruments) low-temperature cell with acetone–dry ice as a coolant. The spectrum of each compound was run several times with different samples at various concentrations. In this way sample decomposition could be monitored and the validity of weak peaks and shoulders established. Some representative spectra for the 1 700—2 100 cm$^{-1}$ region are summarised in the Table.

Nuclear magnetic resonance spectra were run on a JEOL

PFT 100 spectrometer using $C_6D_5CD_3$ as solvent and $SiMe_4$ as an internal standard.

Mass spectra were run on a VG 70-70M mass spectrometer.

## RESULTS

The [NiCo(η-dienyl)(CO)$_4$L] complexes are brown crystalline solids. They are quite stable in the solid state, indefinitely so at −20 °C, except where L is exceptionally volatile *e.g.* $AsMe_3$. Their solutions are stable except when L is an arsine or $P(C_6H_4Me\text{-}o)_2Ph$, or carbon disulphide is the solvent.

*Infrared Spectra.*—For these compounds, up to nine resolved absorption bands may be observed in the 1 700—2 100 $cm^{-1}$ region, A—I. They are due to ν(CO) vibrations.* However the situation is more involved than is apparent at first sight. The absorption bands are often broad with marked shoulders, irregular and asymmetric envelopes, and square tops. These features vary reversibly with temperature. For example, at 25 °C absorption band A of [NiCo(η-$C_5H_4Me$)(CO)$_4${P($C_6H_{11}$)$_2$Ph}] dissolved in hexane has an almost square top due to two major components of comparable intensities at 1 813 and 1 817 $cm^{-1}$ which are not quite resolved. At −78 °C, the absorption band reaches a maximum at 1 812 $cm^{-1}$ but is asymmetric with a marked shoulder at 1 817 $cm^{-1}$.

The absorption bands may be divided into three groups. This is probably an over simplification but it accounts reasonably well for the experimental data. The Group 1 bands comprise D, E, a component of I, and perhaps one of H which is relatively weak. Components of A, C, G, and I form Group 2; and Group 3 are F, H (or the major component of H), B, and a component of A.

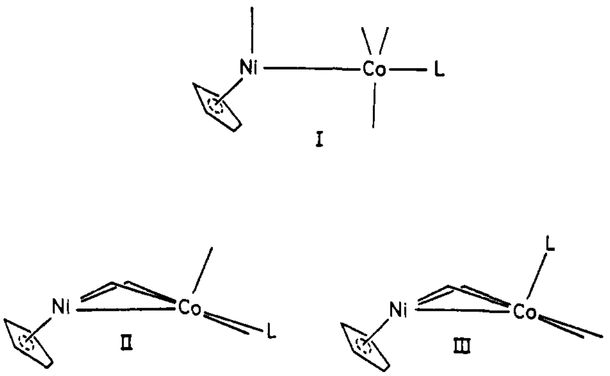
The relative intensities of the absorption bands within each group remain more or less constant, but the relative importances of the groups may vary. Lowering the temperature of the solutions (Table) shifts the equilibria so that (*a*) the intensities of the absorption bands of Group 1 decline with respect to those of Groups 2 and 3, and (*b*) those of Group 3 decline with respect to those of Group 2. Although the Group 2 : Group 3 intensity ratios are virtually independent of solvent, both increase at the expense of those of Group 1 with changes in solvent along the series $CS_2 \geqslant$ hexane > xylene > tetrahydrofuran. Changes of the (η-dienyl) ring or the ligand L do not affect the Group 2 : Group 3 ratio, but these both increase and Group 1 declines along the series dienyl = $C_5H_5 > C_5H_4Me$; L = $P(C_6H_4Cl\text{-}p)_3 > P(C_6H_4F\text{-}p)_3 > P(C_6H_4Cl\text{-}p)_2Ph > PPh_3 > P(C_6H_4OMe\text{-}p)_3 > P(C_6H_4Me\text{-}p)_3$; L = $PPh_3 > P(C_6H_4Me\text{-}o)Ph_2 > P(C_6H_4Me\text{-}o)_2Ph$; † and L = $PPh_3 > AsPh_3$. Also, replacement of one or more phenyl groups of L = $PPh_3$ by an alkyl group brings about a very marked decline in the importance of the Group 1 absorption bands.

*Hydrogen-*1 *N.M.R. Spectra.*—The spectrum of [NiCo(η-$C_5H_5$)(CO)$_4${P($C_6H_4$F-*p*)$_3$}] in perdeuteriotoluene at 20 °C shows three resonances due to the cyclopentadienyl protons, X, Y, and Z (respectively 5.134, 5.151, and 5.156 p.p.m. downfield from $SiMe_4$). Z, unlike X and Y, is not sharp but may have two components of comparable intensities. At 40 °C, Y and Z coalesce whilst X gets much stronger. At even higher temperatures, 60 °C, all three resonances appear to have coalesced to a broad singlet but there is considerable sample decomposition. When the temperature is lowered, X declines very rapidly in importance so that it cannot be observed at −60 °C whilst Z retains its broad character and increases at the expense of Y.

*Mass Spectra.*—These do not show the molecular ion [NiCo(η-dienyl)(CO)$_4$L]$^+$ when L has a very high molecular weight *e.g.* L = $P(C_6H_4F\text{-}p)_3$, but they may be detected when L has a low molecular weight *e.g.* L = $PEt_3$. Otherwise, the fragmentation patterns are of no particular interest.

## DISCUSSION

The [NiCo(η-dienyl)(CO)$_4$L] derivatives are obtained by a nucleophilic displacement of $X^-$ from [Ni(η-dienyl)-LX] by $[Co(CO)_4]^-$. The formation of the Ni–Co bond is accompanied by migration of the phosphine or arsine ligand from nickel to cobalt.[4-6] This unusual reaction has precedents as $[Co(PPh_3)_2(CO)_3]^+$ and $[Co(CO)_4]^-$ give $[Co_2(PPh_3)_2(CO)_6]$ together with a neutral leaving group, CO,[11] and [Ni(η-$C_5H_5$)LBr] and [Fe(η-$C_5H_5$)-$(CO)_2]^-$ form [(η-$C_5H_5$)Ni(μ-CO)$_2$FeL(η-$C_5H_5$)].[12]



The three isomers of [NiCo(η-$C_5H_5$)(CO)$_4$L]. Carbonyl ligands have been omitted for clarity

Infrared spectra show that the [NiCo(η-dienyl)(CO)$_4$L] complexes exist as mixtures of isomers in solution. The Group 1 absorption bands are attributed to the terminal C–O stretching, ν(CO$_t$), vibrations of a species which has no bridging CO ligands. Groups 2 and 3 are due to CO-bridged (μ) forms, A—C to their ν(CO$_\mu$) and the remainder to their ν(CO$_t$) vibrations. The irregular absorption band envelopes suggest that there are more than two of these; they will be referred to collectively as the μ tautomers.

The non-bridged isomer probably has the structure I, Figure, or is a rotamer thereof. The ligand distributions about the Ni and Co atoms are similar to those found in [Ni(η-$C_5H_5$)(PPh$_3$)(CF$_3$)].[13] and [Hg{Co(CO)$_3$(PEt$_3$)}$_2$] [14] respectively. The relative orientations of the two metal-centre moieties would be expected to be such as to reduce interligand interactions across the Ni–Co bond. However, it is quite possible that there is no particularly favourable conformation, and that there is virtually free

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* The remaining regions of the spectra are exceedingly complicated, and a study of them has not helped to solve the present problems. Consequently they will not be discussed here.

† We have not been able to prepare a complex where L = $P(C_6H_4Me\text{-}o)_3$.

rotation about the metal–metal bond as has been found in $[MnCo(CO)_9]$.[15]

A reasonable structure for the unknown species $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}CO)_2Co(CO)_3]$ may be based on the known structures of $[Ni_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2]$,[1] $[Co_2(\mu\text{-}CO)_2(CO)_6]$,[2] and $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}C_2Ph_2)Co(CO)_3]$.[7] From it may be derived two geometrical isomers of the CO-bridged, substituted complexes $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}CO)_2Co(CO)_2L]$, II and III in the Figure. In the solid state the derivatives where $L = PEt_3$,[4] $P(C_6H_4F\text{-}p)_3$,[5] or $P(C_6H_{11})Ph_2$ [6] have structures based on II. However *X*-ray diffraction studies have shown that although they appear similar on a casual appraisal, they are not really so. When $L = P(C_6H_{11})Ph_2$ there is a square-pyramidal arrangement of phosphine and carbonyl ligands about the cobalt atom, whilst when $L = PEt_3$ or $P(C_6H_4F\text{-}p)_3$ it is closer to trigonal bipyramidal. These two forms may exist independently in the solutions for both II and III, or intermediate structures may be adopted which vary in detail depending on L. Furthermore it is noticeable that the clear distinction of absorption bands B from A, F from G, and H from I is only achieved with the ligands $L = P(C_6H_{11})Ph_2$, $P(C_6H_{11})_2Ph$, $PPr^i{}_2Ph$, and to a lesser extent $P(CH_2Ph)Ph_2$ which possess marked axial asymmetry. This suggests that isomers may arise from restricted rotation about the Co–P bonds (*cf.* ref. 16). Finally it should be noted that the ($\eta$-dienyl) ligand may lie above the $Ni(\mu\text{-}CO)_2Co$ plane rather than below it as has been found in the solid state.[4-6]

It is probable that several of these bridged tautomers are present in the solutions with each one giving rise to a distinct i.r. spectrum. The resulting overlap is probably responsible for the breadth and asymmetries of the observed absorption bands, and for their various shoulders. Consequently it is not possible to assign the i.r. spectra in detail. However where sharp symmetrical absorption bands are obtained, their relative intensities are consistent with distributions of CO and L ligands about the Ni–Co core in the $\mu$ tautomers similar to those illustrated for II and III (Figure), and it is probable that these provide the basis for the principal species which are responsible for the absorption bands of Groups 2 and 3.

The $^1H$ n.m.r. spectrum of $[NiCo(\eta\text{-}C_5H_5)(CO)_4\{P(C_6H_4F\text{-}p)_3\}]$ in the cyclopentadienyl region is in general agreement with the i.r. spectral data, and shows that there are three principal species present in solution. The breadth of resonance Z may be due to a coincidence of the cyclopentadienyl resonances of two distinct tautomers; however it persists unchanged over a wide temperature range and so is more likely to be due to a very weak $^{31}P\text{–}C_5H_5$ coupling in one isomer. A correlation of variable-temperature n.m.r. and i.r. spectroscopic data allows the resonance X and the absorption bands of Group 1 to be attributed to isomer I (which declines in importance with decreasing temperature so that its concentration is very low at *ca.* −60 °C), one of the $\mu$ isomers is responsible for Y and Group 3, and the other for Z and Group 2. The interconversion of these geometrical isomers (I, II, and III) is slow on the n.m.r. time scale even at 40 °C. However, the other forms of isomerism discussed above, *i.e.* variations in co-ordination polyhedra about Co and restricted rotation about the Co–P bond, are probably processes which have much lower energies of activation, and which cannot be detected by n.m.r. spectroscopy even at −100 °C.

The solution equilibria may be modified with non-bridged $[NiCo(\eta\text{-dienyl})(CO)_4L]$ isomers declining and $\mu$ isomers increasing in importance (*a*) on lowering the temperature, (*b*) along the solvent series $CS_2 >$ hexane $>$ xylene $>$ tetrahydrofuran, and (*c*) on replacing $C_5H_5$ by $C_5H_4Me$.* (*a*) The temperature effect appears to be quite general with $[Ru_2(\eta\text{-dienyl})_2(CO)_4]$,[17] $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[18] $[FeCo(\eta\text{-dienyl})(CO)_6]$,[19] and $[Co_2(CO)_6(AsR_3)_2]$ [8] behaving in the same way. (*b*) A similar solvent series, but with hexane and $CS_2$ transposed, favours the $\mu$ tautomers of $[Ru_2(\eta\text{-dienyl})_2(CO)_4]$ [20] and $[FeCo(\eta\text{-dienyl})(CO)_6]$ [19] but the non-bridged form of $[Co_2(CO)_6(AsR_3)_2]$.[8] (*c*) For both $[Ru_2(\eta\text{-dienyl})_2(CO)_4]$ [20] and $[FeCo(\eta\text{-dienyl})(CO)_6]$ [19] complexes, replacing $C_5H_5$ by $C_5H_4Me$ also shifts the equilibria towards the $\mu$ isomers.

The ligand L may influence the isomer ratios by its steric and/or electronic effects. Thus the shift in equilibria towards the $\mu$ forms on replacing a Ph group in $L = PPh_3$ by an alkyl group may be a consequence of either {for $[Co_2(CO)_6L_2]$ derivatives where L is a tertiary arsine a similar change has the reverse effect [8]}. On the other hand, changing X in $L = P(C_6H_4X\text{-}p)_3$ probably has negligible steric consequences. The increase in the non-bridged tautomers at the expense of the $\mu$ tautomers along the series $X = Me < H < OMe < F < Cl$ must be primarily electronic in origin, and it parallels the increasing *inductive* electron-withdrawing capacity of X.[21] For the $[Co_2(CO)_6L_2]$ complexes where $L = As(C_6H_4X\text{-}p)Et_2$ [8] the comparable series is $X = Br < F \sim H < Me < OMe$ which parallels the decreasing *overall* electron-withdrawing capacity of X.[21] In both the nickel–cobalt and dicobalt series replacement of $AsPh_3$ by $PPh_3$ favours the species without $\mu$-CO ligands.

Increasing the cone angles [22] of the ligands L along the series $L = PPh_3$, $P(C_6H_4Me\text{-}o)Ph_2$, and $P(C_6H_4Me\text{-}o)_2Ph$ shifts the equilibria dramatically towards $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}CO)_2Co(CO)_2L]$ whereas for $[Co_2(CO)_6L_2]$ more bulky ligands have the opposite effects.[8] This implies that interligand interactions in non-bridged $[NiCo(\eta\text{-}C_5H_5)(CO)_4L]$ must be more important than in the $\mu$ isomers, possibly because L–CO interactions are greater in I than in II or III whilst cross-metal steric interactions appear to be relatively insignificant. This contrasts with the situation in the $[Co_2(CO)_6L_2]$ derivatives where cross-metal interactions are very important.[8]

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* It is assumed that changes in the relative intensities of i.r. absorption bands is a reasonable reflection of changes in the relative concentrations of the species which give rise to them. This has been discussed in ref. 8 and the $^1H$ n.m.r. spectra discussed above support the assumption.

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