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Transition metal-cyanocarbon chemistry

X*. Reactions of monocyanoacetylene and dicyanoacetylene with organometallic compounds of cobalt(I) and nickel(II). Crystal structure of $[\text{Co}(\text{C}\equiv\text{CCN})_2(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$

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Abstract

The reaction of monocyanoacetylene ($\text{HC}\equiv\text{CCN}$) with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ gives the vinylacetylde $[\text{Co}(\text{C}\equiv\text{CCN})(\text{CH}=\text{CH}(\text{CN}))(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$ (**1**) and the diacetylde $[\text{Co}(\text{C}\equiv\text{CCN})_2(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$ (**2**). The crystal structure of the latter has been established by an X-ray diffraction study. Two conformers of **1** are formed in a ratio depending on conditions. In **1** a PPh_3 ligand can be replaced by $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$, which acts as a π -bonded ligand in the product, $[\text{Co}(\text{C}\equiv\text{CCN})(\text{CH}=\text{CH}(\text{CN}))(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-(CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3)]$ (**3**). Treatment of **1** with I_2 gave $(\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{I})_2(\text{P}(\text{C}_6\text{H}_5)_3))$ (**6**) and $\text{CH}(\text{CN})=\text{CH}-\text{C}(\text{CN})=\text{CHI}$ (**5**). The major product of the reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ with dicyanoacetylene ($\text{NCC}\equiv\text{CCN}$) was the 1,6-diphosphorane $(\text{C}_6\text{H}_5)_3\text{P}=\text{C}(\text{CN})\text{C}(\text{CN})=\text{C}(\text{CN})\text{C}(\text{CN})=\text{C}(\text{CN})\text{C}(\text{CN})=\text{P}(\text{C}_6\text{H}_5)_3$. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5(\text{C}\equiv\text{CCN}))]$ (**7**) was isolated from the reaction of monocyanoacetylene with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$. Cyanoalkynes bridge two nickel atoms in $[\mu\text{-(HC}\equiv\text{CCN})][\text{Ni}(\eta^5\text{-C}_5\text{H}_5)]_2$ (**8**) and $[\mu\text{-(NCC}\equiv\text{CCN})][\text{Ni}(\eta^5\text{-C}_5\text{H}_5)]_2$ (**9**), which were formed in the reaction of nickelocene with $\text{HC}\equiv\text{CCN}$ and $\text{NCC}\equiv\text{CCN}$, respectively.

* For part IX see ref. 5

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Introduction

We have previously shown that the cyanoalkynes monocyanoacetylene ($\text{HC}\equiv\text{CCN}$, mca) and dicyanoacetylene ($\text{NCC}\equiv\text{CCN}$, dca) often behave differently from other alkynes towards transition metal complexes, such as hydrido and thiolato complexes of iron, molybdenum and tungsten [1–5]. Because of low steric hindrance together with the presence of $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$ unsaturated systems and the strong electron-withdrawing effect of the CN group, the reactions with cyanoalkynes are often rapid and selective, and give different products from those found in reactions with other alkynes.

Many transition metal complexes of group 9 and 10 play an important role in alkyne dimerization, oligomerization, and polymerization reactions, and in the formation of organometallic complexes which may be precursors for these reactions [6]. It was thus of interest to study the reactions of cyanoalkynes towards cobalt and nickel complexes. Moreover, the presence of the nitrile group provides the potential for the formation of organic species different from those formed by simple cyclisation. We present here the results of a study of the reaction between $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2(\text{PPh}_3)_2]$ (much used previously by Watkasuki [7]) and cyanoalkynes. This cobalt compound usually gave metallacyclopentadienes in reactions with a range of alkynes. Reactions of cyanoalkynes with $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ (which is known to form a variety of complexes with, e.g. hexafluorobutyne [8]) are described. The $18e^-$ $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$ has been also included in the study.

Results and discussion

Reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ with $\text{HC}\equiv\text{CCN}$

Surprisingly (in the light of numerous reports in this area [7]) $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ was found not to react with cyanoalkynes; only traces of polymers formed from these alkynes were observed under the conditions used (stirring for many hours at 40–50 °C, with or without UV irradiation).

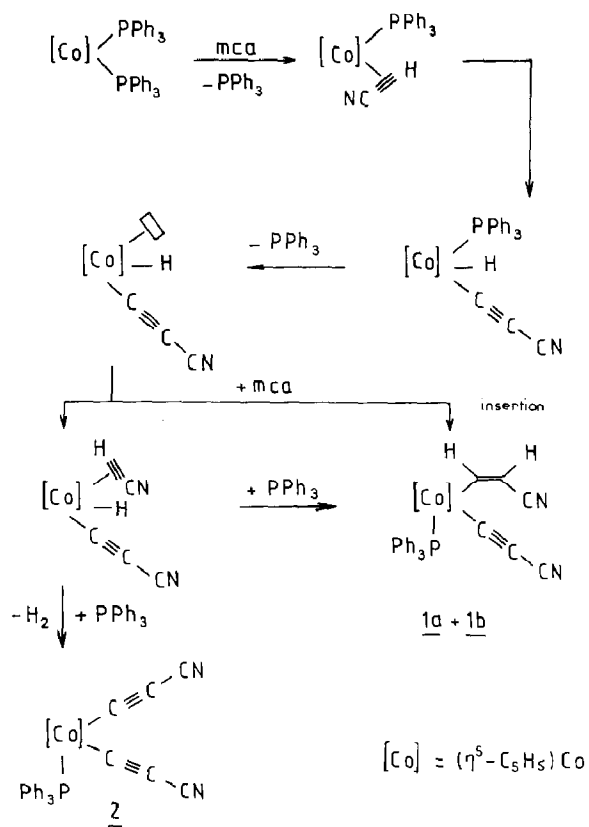
When mca was condensed into a toluene solution of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ frozen in liquid nitrogen, the mixture was allowed to warm to room temperature, and the solvent was then immediately evaporated. Two products were separated by chromatography. One of them was the red vinylacetylide complex $[\text{Co}(\text{C}\equiv\text{CCN})(\text{CH}=\text{CH}(\text{CN}))(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ (**1**), and the other the orange diacetylide $[\text{Co}(\text{C}\equiv\text{CCN})_2(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$ (**2**).

The formation of **1** and **2** must involve oxidative addition of mca and loss of phosphine, in line with the well known lability of phosphines in this type of complex. The hydride acetylide Co^{III} intermediate may be transformed into **1** and **2** (Scheme 1).

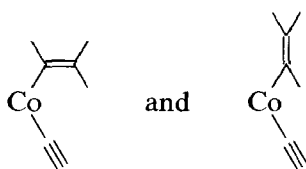
When a toluene solution of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ and mca was stirred for a longer period (3 h) at room temperature, the complex **1** appeared as two isomers **1a** and **1b** in various ratios. The isomers **1a** and **1b** are probably the two conformers shown in Scheme 2, and of a type previously encountered for many vinyl-containing compounds [9,10]. However coalescence could not be clearly observed by NMR spectroscopy, only a broadening of the various signals was observed up to the onset of decomposition at 350 K.

Spectroscopic data for complex **2** (Table 1) suggest the presence of acetylide ligands on cobalt. No acetylenic or olefinic proton peaks appear in the ^1H NMR spectrum (in CDCl_3). Only the ($\eta^5\text{-C}_5\text{H}_5$) (δ 5.07 ppm) and PPh_3 (centered at δ 7.52 ppm) resonances were observed. The strong withdrawal by the CN group and its magnetic anisotropy, together with deshielding due to the metal, result in substantial polarization of the acetylide $\text{C}\equiv\text{C}$ bond in the sense $\text{CoC}_1\equiv\text{C}_2\text{CN}$, analogous to that observed in $[\text{Fe}(\text{C}\equiv\text{CCN})(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ [5] (105.58, C_1 ; 87.39–87.34 ppm, C_2 ; $^3J(\text{C-P})$ 3.6 Hz) (Table 2).

Other cobalt acetylides, involving hexa- [11], tetra- [12] and mono-acetylide derivatives [13], have been described in literature, but no example of a cyclopentadienylcobalt acetylide was previously known. We thus decided to determine the crystal structure of **2**. The complex is pseudooctahedral rather than pseudotetrahedral (Fig. 1). In fact, the three angles $\text{C}(24)\text{-Co-C}(27)$, $\text{C}(24)\text{-Co-P}$ and $\text{C}(27)\text{-Co-P}$ are close to 90° (mean 93°) indicating that the three orbitals engaged in bonds with the ($\eta^5\text{-C}_5\text{H}_5$) cycle are little perturbed (Table 3). This interpretation is consistent with Davies' conclusions about the geometry of the complexes of the type $[\text{Co}(\text{PPh}_3)\text{MLX}]$ [14]. However, the orientation of the phenyl groups does not follow the geometrical rules proposed by Davies. The plane of the $\text{C}(13)\text{-C}(18)$



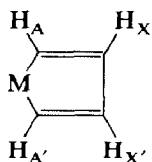
Scheme 1



Scheme 2

phenyl group is not parallel to the plane of the two acetylide ligands (the angle between these planes is 65.8°) but the phenyl group situated at the opposite of the C(24)–N(2) acetylide is nearly parallel to the plane of the acetylides (the value of the dihedral angle is 8.5°). The Co–C(24) and Co–C(27) (involving sp -hybridized acetylide carbons) bond lengths, viz 1.87(1) Å, are very short, as expected. A Co–C(sp^2) distance of 1.97(1) Å (+0.1 Å) has been observed in a σ -vinylic cobalt(III) complex formed by the action of (*p, p'*-DTT)(1,1-bis-(*p*-chlorophenyl-2,2,2-trichloroethane) on cobaloxime (bis(dimethylglyoximato)pyridinecobalt(I) [15] and typical Co–C (sp^3) distances are close to 2.04–2.05 Å [16]. The (C≡C) bond lengths are normal (1.192(14) and 1.198(10) Å) [17,18]. Their mean value is nearly the same as the 1.202 Å proposed for a C≡C triple bond uncoordinated to a metal [19]. However the molecular parameters determined by X-ray diffraction are less sensitive to the effects of electronic influences than the spectroscopic parameters. To our knowledge, the $\nu(\text{C}\equiv\text{C})$ vibration frequency is the lowest one (2045 cm^{-1}) observed for acetylides. For $[\text{Fe}(\text{C}\equiv\text{CCN})(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ it is 2080 cm^{-1} [5] and in iron acetylides of the type $[\text{Fe}(\text{C}\equiv\text{CR})(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ where R is CH_3 , C_4H_9 and C_6H_5 it is in the range $2105\text{--}2140\text{ cm}^{-1}$ [20,21]. The importance of the nature of the ligands is evident also for manganese complexes, the $\nu(\text{C}\equiv\text{C})$ frequency decreasing from 2119 in $[\text{Mn}(\text{CO})_5(\text{C}\equiv\text{CPh})]$ to 2058 cm^{-1} in $[\text{Mn}(\text{CO})(\text{dppm})_2(\text{C}\equiv\text{CPh})]$ (dppm = diphenylphosphinomethane) [22].

As stated above, complex 1 was isolated as a mixture of two isomers. In the ^1H NMR spectra, the peaks in the 5–7 ppm range are consistent with two *cis*-olefinic protons in a (*Z*)(CoCH=CH(CN)) entity. The values of the $J(\text{H}–\text{H})$ coupling constants ($\sim 10\text{ Hz}$) show that the products cannot be cobaltacyclopentadienyl species, such as are usually formed in the reactions of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ with alkynes. Various coupling constants observed for metallacyclopentadienyl species [23] are shown below.



$$(^3J_{AX} 5.3; ^4J_{AX'} 2.1; ^4J_{AA'} 0.3; ^3J_{XX'} 3.6\text{ Hz})$$

With monosubstituted alkynes, the protons are usually in the positions A and X' (or A' and X). For other metallacyclopentadienylchromium complexes of the type $[(\mu\text{-C}_4\text{R}_2\text{R}'_2)\text{Cr}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})]$ (R = C_6H_5 , CH_3 , R' = H) the $^4J(\text{H}–\text{H})$ coupling constants fall in the range 2.5–3 Hz [24].

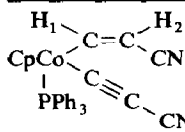
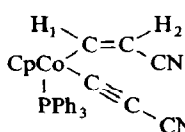
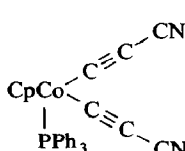
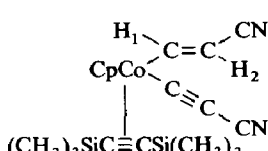
The presence of two carbon atoms, each bearing one proton, is confirmed by ^{13}C NMR spectroscopy ($^1J(\text{C}_\alpha\text{-H})$ 168.4, $^1J(\text{C}_\beta\text{-H})$ 174.5 Hz) (Table 2). For each isomer, two doublets (coupling with ^{31}P) assignable to acetylide carbon atoms appear.

In the case of complex **2**, only the C_2 carbon atom is coupled, weakly, to phosphorus ($^3J(\text{C}_2\text{-P})$ 3.6 Hz). In contrast, this coupling is large in **1a** ($^3J(\text{C}_2\text{-P})$ 12.3 Hz), whereas the $^2J(\text{C}_1\text{-P})$ coupling constant is normal (11.3 Hz). Moreover, in the case of the σ -vinylic ligand there is a weak P-C coupling between the sole C_α carbon atom of the minor isomer **1b**, whereas in ruthenium complexes the vinylic carbon atoms in the ligand $\text{C}(\text{CO}_2\text{CH}_3)=\text{C}(\text{CO}_2\text{CH}_3)\text{Ph}$, for example, are coupled to the phosphorus nuclei of a phosphine ligand ($^2J(\text{P-C})$ 13.3 Hz and $^3J(\text{P-C})$ 3.7 Hz) [25]. Interpretation of the carbon-phosphorus coupling in these compounds seems to be a complex problem; because the values of the coupling constants depend on several factors such as the σ -character of the bonds and the symmetry and geometrical parameters of the molecules.

The ^{13}C signal at 118.22 ppm (**1a**) shows coupling with a proton ($J(\text{C-H})$ 14.5 Hz). This coupling is consistent with a $^3J(\text{C-H})$ coupling between the carbon atom

Table 1

 ^1H and ^{31}P spectroscopic data (δ in ppm, J in Hz) (CDCl_3 solutions) ^a

Compound	H^1	H^2	Cp	PPh_3	Others	^{31}P
 (1a) ^b	6.45 dd $^3J(\text{H-H})10.2$ $^3J(\text{H-P})4.0$	5.42 d $^3J(\text{H-H})10.2$	4.83	7.40 m		56.7
 (1b) ^b	6.84 dd $^3J(\text{H-H})9.6$ $^3J(\text{H-P})3.6$	5.82 d $^3J(\text{H-H})9.6$	4.71	7.40 m		58.9
 (2)			5.07	7.52 m		52.9
 (3)	6.89 d $^3J(\text{H-H})16.2$	5.64 d $^3J(\text{H-H})16.2$	5.03 s		0.2 0.25 CH_3	

^a Cp: ($\eta^5\text{-C}_5\text{H}_5$); s: singlet; d: doublet; dd: doublet of doublets; m: multiplet. ^b **1a** and **1b** are two different conformers (see text, Scheme 2).

Table 2

 ^{13}C NMR spectroscopy (δ in ppm, J in Hz) (CDCl_3 solutions)

Compound	Cp	C ¹	C ²	C _{α}	C _{β}	CN(C _{β})	CN(C ²)	Others
$\begin{array}{c} \text{H} \\ \\ \text{C}_\alpha = \text{C}_\beta - \text{CN} \\ \\ \text{CpCo} - \text{C}^1 \\ \\ \text{PPh}_3 \equiv \text{C}^2 - \text{CN} \end{array}$	84.88	120.29	82.45	135.42	98.51	118.22	114.92	
	84.85 $J(\text{C-P}):2.8$	120.14 $^2J(\text{C-P}):11.3$ $^3J(\text{C-H}):13.4$	82.28 $^3J(\text{C-P}):12.3$	$^1J(\text{C-H}):168.4$	$^1J(\text{C-H}):174.5$	$^2J(\text{C-H}):14.5$		
(1a) ^a	83.65	121.70	78.64	138.35	103.25	118.55	114.49	
	83.61 $J(\text{C-P}):2.8$	121.53 $^2J(\text{C-P}):12.4$	78.48 $^3J(\text{C-P}):11.4$					
(1b) ^a	91.86	105.58	87.39				106.1	
	91.84 $J(\text{C-P}):1.8$		87.34 $^3J(\text{C-P}):3.6$					
(2)	81.64	110.90	80.66	147.08	93.91	$^1J(\text{C-H}):170.0$	$^1J(\text{C-H}):170.0$	118.80 C \equiv CSi(CH ₃) ₃ 118.7 1.06 CH ₃ 0.73
				$^1J(\text{C-H}):170.0$		$^1J(\text{C-H}):170.0$		
(3)								

^a **1a** and **1b** are two conformers (see text, Scheme 2) ^b Not observed; (¹H) coupling was recorded with the pure **1a** conformer only; PPh₃; δ (¹³C) ~ 130 ppm.

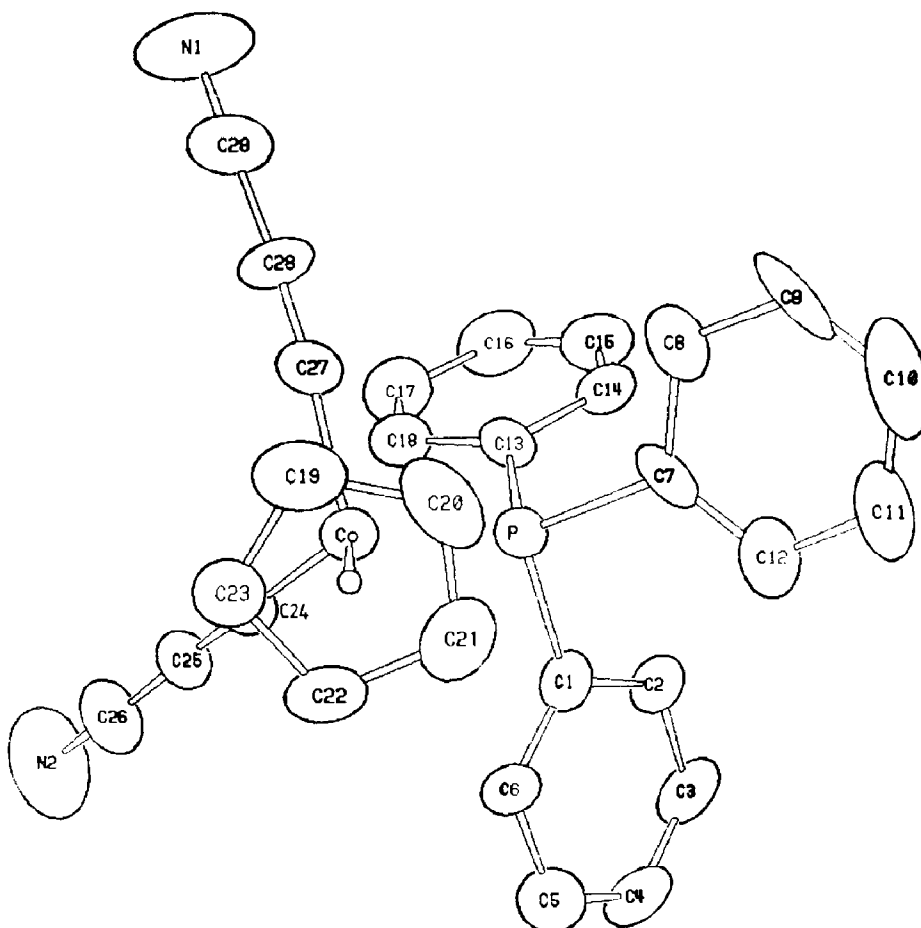
Table 3

Selected bond lengths (Å) and bond angles (°) for $[\text{Co}(\text{C}\equiv\text{CCN})_2(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$ (**2**)

Co–C(24)	1.857(12)	C(24)–Co–C(27)	95.1(5)
Co–C(27)	1.877(7)	C(24)–Co–P	93.4(3)
Co–P	2.232(3)	C(27)–Co–P	90.7(4)
C(24)–C(25)	1.192(14)	Co–C(24)–C(25)	174(1)
C(27)–C(28)	1.198(10)	Co–C(27)–C(28)	173(1)
C(25)–C(26)	1.358(15)	C(24)–C(25)–C(26)	178(1)
C(28)–C(29)	1.363(13)	C(27)–C(28)–C(29)	175(1)
C(26)–N(2)	1.152(14)	C(25)–C(26)–N(2)	180(1)
C(29)–N(1)	1.146(12)	C(28)–C(29)–N(1)	178(1)

of the CN group attached to the C_β atom and a proton situated *trans* to it on the C_α atom [26]. There is a similar $^3J(\text{C}_1\text{-H})$ coupling with the proton on the C_α atom (**1a**).

The infrared spectrum of isomer **1a** shows three vibration bands in the 2100–2200 cm^{-1} region. Those with the highest frequencies (2230(w) and 2200(m) cm^{-1}) correspond to the $\nu(\text{C}\equiv\text{N})$ vibration of the acetylide and vinylic ligands. In this case,

Fig. 1. ORTEP drawing of $[\text{Co}(\text{C}\equiv\text{CCN})_2(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$ (**2**).

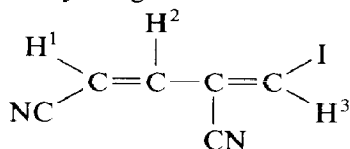
the band of medium intensity at 2145 cm^{-1} may be assigned to the $\nu(\text{C}\equiv\text{C})$ vibration of the acetylide. Comparison of that frequency with the chemical shift of the C_1 carbon in **1** clearly indicates that the ^{13}C NMR data cannot be interpreted solely in terms of the inductive effect, and reveals the significance of the paramagnetic contribution to the overall shielding. In the case of the complex **2**, an important three-center interaction involving one antibonding in-plane π orbital of each carbon atom C_1 and one symmetry adapted d orbital (π type) of cobalt may lead to an increase in the spatial expansion of p orbitals on carbon (r^{-3} term in the Jameson and Gutowsky equation [27]), and so to a decrease in σ_{para} (higher fields). In complex **1**, which contains the σ -vinylic ligand, such in-plane interaction may be less extended or absent, so that there is a smaller extension of the p orbitals and so a shift of the signal to lower field. In the absence of theoretical calculations, especially on the role of ΔE and $\langle r \rangle$ terms [27] in the paramagnetic perturbation, we cannot offer a complete interpretation of the data.

In the absence of suitable single crystals, in order to provide indirect evidence of the presence of the σ -vinylic and acetylide ligands formed for the first time in the reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ with alkynes*, several reactions were carried out. The action of S_8 on **1** resulted in decomposition of the complex and formation of SPPH_3 , whereas in the case of cobaltacyclopentadienes, derivatives of thiophene are formed generally [28]. The various isomers of dicyanothiophene are known [29].

Cobaltacycloheptatrienes or benzene derivatives are usually formed in reactions of cobaltacyclopentadienes with alkynes [6]. Decomposition takes place when **1** is mixed with, for example, diphenylacetylene or dimethylacetylene dicarboxylate. Only $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, known to take part readily in cyclisation reactions with dienes and diynes [30], reacts with **1**, to give the complex $[\text{Co}(\text{C}\equiv\text{CCN})(\text{CH}=\text{CH}(\text{CN}))(\eta^2\text{-(CH}_3)_3\text{SiC}\equiv\text{CSi(CH}_3)_3)(\eta^5\text{-C}_5\text{H}_5)]$ (**3**). The ^1H NMR spectrum of the product indicates that the phosphine ligand has been replaced by the alkyne. Heating (50°C) is necessary for the reaction, which involves *cis-trans* isomerization of the two vinylic protons ($^3J(\text{H-H})$ 16.2 Hz) [26]. The ^{13}C NMR spectra suggests that there is an increased polarization of the $\text{C}\equiv\text{C}$ bond, probably because of the absence of phosphine. The ^{13}C signals for CN are not observed.

The infrared spectrum of **3** in the $2100\text{--}2200\text{ cm}^{-1}$ region consists of a disymmetrical medium band (2203 cm^{-1}) probably incorporating both of the $\nu(\text{C}\equiv\text{N})$ vibration bands, and a weak band (2150 cm^{-1}), possibly assignable to the $\nu(\text{C}\equiv\text{C})$ acetylide vibration.

Addition of iodine to complex **1** was expected to give vinylacetylene $\text{CH}(\text{CN})=\text{C}(\text{H})\text{C}\equiv\text{CCN}$ by coupling of the two ligands, but that product was not detected. Complex $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{I})_2(\text{PPh}_3)]$ (**6**) was formed very quickly and quantitatively, and a small amount of an organic product **5** was sublimed out. The analysis agrees with the following formulation:

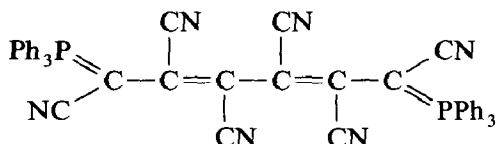


* As this paper was being written, another appeared in which reactions of $\text{CoBr}(\text{PMe}_3)_3$ with the terminal alkynes $\text{HC}\equiv\text{C-t-Bu}$, $\text{HC}\equiv\text{CPr}$ and $\text{HC}\equiv\text{CPh}$ are described. The vinylacetylide complex $[\text{Co}(\text{C}\equiv\text{C-t-Bu})(\text{HC}=\text{CH-t-Bu})(\text{MeCN})(\text{PMe}_3)_3]\text{BPh}_4$ was obtained, and its crystal structure determined [37].

^1H NMR spectrum reveals the presence of *cis*-vinylic protons (H^1 : doublet centered at 5.44 ppm: $^3J(\text{H}^1-\text{H}^2)$ 11.8 Hz; H^2 : doublet of doublets centered at 6.91 ppm; $^3J(\text{H}^1-\text{H}^2)$ 11.8; $^4J(\text{H}^2-\text{H}^3)$ 1.3 Hz; H^3 : doublet centered at 6.81 ppm; $^4J(\text{H}^2-\text{H}^3)$ 1.3 Hz). The chemical shift of H^1 is consistent with the shielding effect of the vicinal CN group, and those of H^2 and H^3 are as expected. When solutions (CDCl_3) of **5** were exposed to light, they became violet after a few hours, indicating the presence of iodine. The mass spectrum showed the molecular ion at $m/1$, and additional peaks at m/e 127 (I^+) and 103 ($M - \text{I} +$).

Reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ with $\text{NCC}\equiv\text{CCN}$

The reaction of dca with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$ in toluene gives triphenylphosphine, a very small amount of an organometallic product for which only ^1H NMR data could be obtained (5.17 ppm(s)($\eta^5\text{-C}_5\text{H}_5$), 7.5 ppm (m)(PPh_3); corresponding to the metallacycle $[\text{Co}(\text{C}(\text{CN})=\text{C}(\text{CN})\text{C}(\text{CN})=\text{C}(\text{CN}))(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)]$, and of an organic product (yield 80%). Analytical data and the melting point correspond to the polymer



which was made previously in a different way, not involving an organometallic complex [31].

Reaction of $[\text{Co}(\eta^4\text{-C}_5\text{H}_6)(\eta^5\text{-C}_5\text{H}_5)]$ with $\text{HC}\equiv\text{CCN}$

A synthesis method based on that used by Cordes [32] for the preparation of cobaltocene gave the cyclopentadienyl-cyclopentadienecobalt in good yield (see Experimental section); this complex was previously prepared by the reduction of a cobalticinium halide with NaBF_4 or LiAlH_4 [33]. The orange product formed in the reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$ with mca was separated from alkyne polymers by chromatography. The analytical and spectroscopic data are consistent with the formulation $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5(\text{C}\equiv\text{CCN}))]$, produced formally by the substitution of one of the geminal protons of the ($\eta^4\text{-C}_5\text{H}_6$) ligand by the ($\text{C}\equiv\text{CCN}$) acetylide group, as in the reactions of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$ in CHCl_3 and CH_2Cl_2 in which $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5(\text{CCl}_3))]$ and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5(\text{CHCl}_2))]$ are formed. This again shows the acidic character or the strong polarization of mca. No reaction occurred with dca, except for the formation of a small amount of alkyne polymer.

Reaction of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ with cyanoalkynes

The reactions between $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ and cyanoalkynes are very slow, and heating is necessary. In addition to a large amount of black insoluble polymer, only one new organometallic complex was isolated, whereas with hexafluorobutyne, for instance, four different products were formed [8]. Analytical and spectroscopic data are consistent with the formulation $[\mu\text{-}(\text{RC}\equiv\text{CCN})][\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ ($\text{R} = \text{H}$, **8**; CN , **9**), containing a metal-metal bond.

Experimental

The reactions were performed under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and purged with nitrogen before use. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ was prepared from $[\text{CoCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3]$ by a published method [34]. $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$ was obtained by a procedure similar to that used for $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]$ [32] (vide infra). Monocyanoacetylene and dicyanoacetylene were made (in 70% yield) by a published method from the corresponding amides [35]. The other products were from commercial sources.

The ^1H , ^{13}C and ^{31}P NMR spectra were recorded on a JEOL-JNM-FX 100 or on a Bruker AC 300 spectrometer. Chemical shifts (δ values) are relative to internal TMS (^1H , ^{13}C) or external aqueous H_3PO_4 (^{31}P). Infrared spectra of samples as KBr pellets, Nujol mulls on CsI plates, or CH_2Cl_2 solutions, were recorded on a Perkin Elmer 1430 spectrophotometer. Mass spectra were recorded at 70 eV on a Varian MAT 8M spectrometer at the Faculté des Sciences of Rennes (complexes **7**, **8** and **9**) or on a RIBERMAG R10-10 spectrometer coupled with a CPG chromatograph (column 25 m SE 52) at the Faculté de Médecine of Brest (compound **5**).

Microanalysis were performed at the Centre de Microanalyses of the CNRS.

Reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ with $(\text{HC}\equiv\text{CCN})$

Freshly prepared monocyanoacetylene (30 mmol) was condensed into a toluene solution (~ 100 ml) of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ (7 g, 10.8 mmol) frozen in liquid nitrogen. The mixture was stirred (30 min) as the temperature was allowed to rise slowly. The solution became orange and then rapidly turned deep-red. The solvent was evaporated off, and the solid residue was chromatographed on a silica gel column. Elution with a dichloromethane/hexane mixture (1/2 in volume) gave PPh_3 . A second band containing the red $[\text{Co}(\text{C}\equiv\text{CCN})(\text{CH}=\text{CH}(\text{CN}))(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$ (**1**) was eluted with dichloromethane (yield 65%), and $[\text{Co}(\text{C}\equiv\text{CCN})_2(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$ (**2**) was obtained as a yellow band by elution with a mixture dichloromethane/THF (95/5) (yield 20%). Small amounts of alkyne polymers were recovered by chromatography (with methanol as eluent).

Complex 1. Analysis. Found: C, 70.6; H, 4.9; Co, 11.4; N, 5.7; P, 6.2. $\text{C}_{29}\text{H}_{22}\text{CoN}_2\text{P}$ calc.: C, 71.32; H, 4.54; Co, 12.07; N, 5.74; P, 6.34%. Infrared (cm^{-1}), KBr pellets, isomer **1a**: 2230(w), 2200(m) $\nu(\text{C}\equiv\text{N})$; 2145(m) $\nu(\text{C}\equiv\text{C})$; 1570(m) $\nu(\text{C}=\text{C})$.

Complex 2. Analysis. Found: C, 70.0; H, 4.3; Co, 12.8; N, 5.7; P, 6.4. $\text{C}_{29}\text{H}_{20}\text{CoN}_2\text{P}$ calc.: C, 71.61; H, 4.14; Co, 12.12; N, 5.76; P, 6.37%. Infrared (cm^{-1}), KBr pellets: 2200 (m) $\nu(\text{C}\equiv\text{N})$; 2040(m) $\nu(\text{C}\equiv\text{C})$. Good single crystals were obtained by recrystallization from acetone.

When the mixture of mca and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ was stirred for a longer period (3 h) before toluene was evaporated off, a second isomer **1b** was formed alongside **1a**. However in some cases equal amounts of **1a** and **1b** were formed.

*Formation of $[\text{Co}(\text{C}\equiv\text{CCN})(\text{CH}=\text{CH}(\text{CN}))(\eta^2\text{-}(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3)(\eta^5\text{-C}_5\text{H}_5)]$ (**3**)*

A solution of 660 mg (1.35 mmol) of **1** and 250 mg (1.5 mmol) of $(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$ in toluene was stirred for 12 h at 50°C , during which the colour changed from red to brown. Decomposition products were removed by filtration and the solvent evaporated. The solid residue was dissolved in dichloro-

methane and chromatographed on a neutral alumina column. PPh_3 was separated with hexane as eluent. Complex **3** was eluted as a yellow band with CH_2Cl_2 (yield 20%). A mixture of CH_2Cl_2 and THF (99/1) gave a red band, which after evaporation of the solvent gave an unstable and unidentified product (yield 20%).

Complex **3**. Analysis. Found: C, 56.8; H, 6.2; Co, 14.4; N, 7.3. $\text{C}_{19}\text{H}_{25}\text{CoN}_2\text{Si}_2$ calc.: C, 57.55; H, 6.36; Co, 14.86; N, 7.06%. Infrared (cm^{-1}), KBr pellets; 2210 sh, 2203(m) $\nu(\text{C}\equiv\text{N})$; 2150 (w) $\nu(\text{C}\equiv\text{C})$.

Reaction of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ with $\text{NCC}\equiv\text{CCN}$

Freshly prepared dicyanoacetylene (10 mmol) was condensed into a toluene solution (40 ml) of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)_2]$ (2.5 g, 3.85 mmol) frozen in liquid nitrogen. The mixture was stirred for 30 min as the temperature was allowed to rise slowly and the solution turned to brown. The solvent was evaporated off, and the solid residue was chromatographed on a silica gel column. Elution with a dichloromethane/hexane mixture (1/2 in volume) gave PPh_3 . A very small amount of an organometallic complex (possibly $[\text{CoC}(\text{CN})=\text{C}(\text{CN})\text{C}(\text{CN})=\text{C}(\text{CN})(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$, see Discussion) was eluted with dichloromethane, followed by the red 1,6-diphosphorane $(\text{C}_6\text{H}_5)_3\text{P}=\text{C}(\text{CN})\text{C}(\text{CN})=\text{C}(\text{CN})\text{C}(\text{CN})=\text{C}(\text{CN})\text{C}(\text{CN})=\text{P}(\text{C}_6\text{H}_5)_3$. Analysis. Found: C, 75.6; H, 4.4; N, 11.4; P, 8.2. $\text{C}_{48}\text{H}_{30}\text{N}_6\text{P}_2$ calc.: C, 76; 59; H, 4.02; N, 11.16; P, 8.23%. Melting point: 240 °C.

*Reaction of $[\text{Co}(\text{C}\equiv\text{CCN})(\text{CH}=\text{CH}(\text{CN}))(\eta^5\text{-C}_5\text{H}_5)(\text{P}(\text{C}_6\text{H}_5)_3)]$ (**1**) with I_2*

An equimolar mixture of complex **1** and iodine in toluene at room temperature was stirred for 2 h, during which the colour of the solution changed from red to dark green. After filtration the solvent was evaporated off. Colourless crystals of **5** were sublimed out under vacuum at 60 °C from the solid (yield < 5%). The residual dark green solid **6**, $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{I})_2(\text{PPh}_3)]$, was washed with hexane and dried under vacuum.

Compound **5**. MS(m/e). 230, calc. for $\text{CH}(\text{CN})=\text{CHC}(\text{CN})=\text{CHI}$: 230; other peaks at 229: ($M - \text{H}$)⁺; 127: I⁺; 103: ($M - \text{I}$)⁺; 102: $(\text{CH}(\text{CN})=\text{CHC}\equiv\text{CCN})^+$. ¹H NMR (see Discussion).

Complex **6**. Analysis. Found: C, 43.3; H, 3.3; Co, 9.5; I, 39.5; P, 5.1; $\text{C}_{23}\text{H}_{20}\text{CoI}_2\text{P}$ calc.: C, 43.16; H, 3.15; Co, 9.21; I, 39.65; P, 4.84%.

Preparation of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$

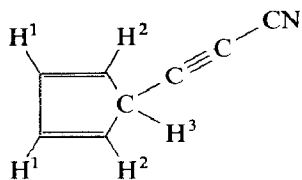
To a solution of (NaC_5H_5) in THF, prepared by distillation of an excess of C_5H_6 (12 ml) on 2 g of Na, were added 20 g of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$. The mixture was stirred for 2 h at 50 °C. NaCl was removed by filtration through alumina, and the solvent was evaporated off. Yellow crystals of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$ (6 g) were sublimed at 100 °C (oil bath) from the solid residue.

*Preparation of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5(\text{C}\equiv\text{CCN}))]$ (**7**)*

A solution of 2 g (10.5 mmol) of $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)]$ and 18 mmol of $\text{HC}\equiv\text{CCN}$ in THF was kept for 10 h at -90 °C during which an insoluble black solid (alkyne polymers) separated. After filtration, the solvent was evaporated off, and an orange fraction containing the compound **7** was eluted with hexane from a Florisil column (yield 10%). Soluble alkyne polymers were eluted with THF.

Complex **7**: M(m/e): 239, calc.: 239; other peaks at 189: $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ and 124: $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)]^+$. Infrared (cm^{-1}), Nujol: 2260 $\nu(\text{C}\equiv\text{N})$; 2190 $\nu(\text{C}\equiv\text{C})$. ¹H

NMR (δ ppm): 4.31 (5H)(η^5 -C₅H₅); 4.8(H¹) pseudotriplet; 2.92 (H³) triplet; 2.10 (H²) pseudoquartet. The assignment of the various peaks of the η^4 -cyclopentadiene ligand were based on data from selective irradiation.



*Preparation of $[\mu\text{-(HC}\equiv\text{CCN)}][\text{Ni}(\eta^5\text{-C}_5\text{H}_5)]_2$ (**8**)*

A solution of 1.8 g (9.5 mmol) of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ and 11 mmol of HC \equiv CCN in THF or toluene was stirred at 75 °C for 55 h. After filtration off of a black precipitate (alkyne polymers), the solvent was evaporated off and the residue was chromatographed on a Florisil column. Elution with dichloromethane gave the starting $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$. Complex **8** was eluted as a green band with dichloromethane and recrystallized from a CH₂Cl₂/hexane mixture (yield 20%). Red polymers of the cyanoalkyne were eluted with pure THF.

Compound **8**. Analysis. Found: C, 52.4; H, 3.9; N, 5.0; Ni, 39.5; C₁₃H₁₁NNi₂ calc.: C, 52.50; H, 3.70; N, 4.70; Ni, 39.05%. ¹H NMR (CDCl₃)(δ ppm): 5.38 (10 H) (η^5 -C₅H₅); 5.42 (HC \equiv CCN). MS(*m/e*): 299, molecular peak with one ⁶⁰Ni atom and one ⁵⁸Ni atom; 297, molecular peak with two ⁵⁸Ni atoms.

*Preparation of $[\mu\text{-(NCC}\equiv\text{CCN)}][\text{Ni}(\eta^5\text{-C}_5\text{H}_5)]_2$ (**9**)*

A solution of 2 g (10.6 mmol) of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$ and 16 mmol of dca in toluene was stirred at room temperature for 3 days. A black precipitate (alkyne polymers) was filtered off, the solvent evaporated, and the residual solid dissolved in CH₂Cl₂. Elution with dichloromethane (Florisil column) gave successively the starting $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2]$, a small amount of a red product that was not identified, and complex **9** (yield 10%). Red alkyne polymers were eluted with pure THF.

Complex **9**: ¹H NMR (CDCl₃)(δ ppm): 5.54 (η^5 -C₅H₅); MS(*m/e*): molecular peaks at 326, 324 and 322, with two ⁶⁰Ni atoms, one ⁶⁰Ni and one ⁵⁸Ni atoms and two ⁵⁸Ni atoms, respectively.

X-ray structure analysis of 2

An orange crystal grown from acetone solution was mounted on an Enraf-Nonius CAD-4 four circle diffractometer. The unit cell was determined and refined from 25 randomly selected reflections obtained by use of the CAD-4 automatic routines. Crystal data for **2**: orthorhombic, space group *Pna*2₁ (No. 33), *a* 20.691(8), *b* 7.810(3), *c* 14.597(6) Å, *U* 2359 Å³, $\mu(\text{Mo-K}\alpha)$ 8.1 cm⁻¹, *Z* = 4. The intensities of 1694 independent reflections were measured in an ω -2 θ scan (θ_{min} 1°, θ_{max} 23°) but only 1028 reflections with *I* > 3 σ (*I*) were used in the solution and refinement of the structure. All calculations were carried out by use of the Enraf-Nonius SDP package [36]. The structure was solved and refined (178 variables) by conventional three-dimensional Patterson, difference Fourier, and full-matrix least squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms calculated by the "Hydro" program of SDP and these atoms were included in the final calculations, with *B*_{iso} fixed at 5.0 Å². The

Table 4

Positional parameters and their estimated standard deviations for **2**^a

Atom	x	y	z	B(Å ²)
Co	0.12837(5)	0.2269(1)	0.142	2.59(2)
P	0.1312(1)	0.0600(3)	0.2665(1)	2.46(4)
N(1)	0.3928(4)	0.340(1)	0.1134(8)	7.9(3)
N(2)	0.1051(6)	-0.290(1)	-0.1165(7)	9.2(3)
C(1)	0.0637(4)	-0.088(1)	0.2785(5)	2.8(2)
C(2)	0.0638(4)	-0.207(1)	0.3512(5)	3.1(2)
C(3)	0.0116(4)	-0.320(1)	0.3603(6)	3.7(2)
C(4)	-0.0394(4)	-0.313(1)	0.3015(7)	4.1(2)
C(5)	-0.0405(4)	-0.195(1)	0.2323(6)	4.3(2)
C(6)	0.0121(4)	-0.083(1)	0.2188(6)	3.1(2)
C(7)	0.1281(4)	0.186(1)	0.3717(5)	3.4(2)
C(8)	0.1829(5)	0.286(1)	0.3962(6)	4.8(2)
C(9)	0.1791(6)	0.386(1)	0.4748(6)	6.4(3)
C(10)	0.1245(6)	0.397(1)	0.5248(6)	6.5(3)
C(11)	0.0707(6)	0.303(1)	0.5012(6)	5.4(3)
C(12)	0.0725(5)	0.199(1)	0.4252(6)	4.3(2)
C(13)	0.2010(3)	-0.079(1)	0.2805(5)	2.9(2)
C(14)	0.2250(4)	-0.120(1)	0.3669(6)	3.4(2)
C(15)	0.2725(4)	-0.246(1)	0.3785(7)	4.4(2)
C(16)	0.2973(4)	-0.326(1)	0.3048(7)	4.8(2)
C(17)	0.2748(4)	-0.283(1)	0.2168(7)	4.3(2)
C(18)	0.2277(4)	-0.162(1)	0.2056(7)	3.4(2)
C(19)	0.1281(4)	0.488(1)	0.1141(6)	4.7(2)
C(20)	0.1037(5)	0.460(1)	0.2016(7)	4.7(2)
C(21)	0.0476(4)	0.358(1)	0.1934(7)	4.5(2)
C(22)	0.0394(4)	0.321(1)	0.1002(6)	3.6(2)
C(23)	0.0899(4)	0.401(1)	0.0515(6)	3.6(2)
C(24)	0.1245(4)	0.043(1)	0.0622(5)	3.3(2)
C(25)	0.1150(4)	-0.067(1)	0.0057(6)	3.6(2)
C(26)	0.1116(5)	-0.188(1)	-0.0603(7)	5.4(3)
C(27)	0.2189(3)	0.2420(9)	0.1421(9)	3.0(1)
C(28)	0.2759(3)	0.266(1)	0.1360(9)	3.8(2)
C(29)	0.3395(4)	0.304(1)	0.1229(8)	4.5(2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$.

final residuals were $R = 0.032$, $R_w = 0.03$, $60F = 1.022$. Refinements carried out for the enantiomer gave similar R and R_w factors, and so the two forms are equivalent. The weighting scheme employed was $w^{-1} = \frac{1}{4}[\sigma(I)/(I) + 0.05(I)^2]$. The final atomic coordinates are listed in Table 4.

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