Cobalt Metallocycles. Part 10.† Preparation and *X*-Ray Structures of Two Isomeric Dicyanocobaltacyclopentanes ‡

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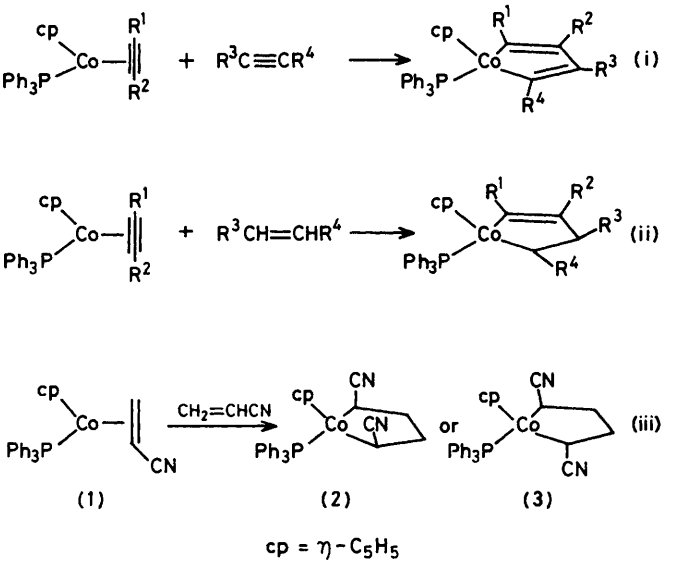
Two isomeric 1,4-dicyanocobaltacyclopentanes, $[Co(\eta\text{-}C_5H_5)(C_6H_6N_2)(PPh_3)]$, have been prepared by the reaction of the acrylonitrile complex $[Co(\eta\text{-}C_5H_5)(CH_2{=}CHCN)(PPh_3)]$ (1) with free acrylonitrile and were characterized by single-crystal *X*-ray analysis. The *cis* isomer (2) crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions a = 11.464(3), b = 13.782(3), c = 9.277(2) Å, α = 87.48(2), β = 110.23(1), γ = 84.26(2)°, Z = 2, and R = 0.067 for 4 238 independent observations. Crystals of the *trans* isomer (3) are orthorhombic, space group *Fdd*2, with a = 12.821(1), b = 65.833(20), c = 11.470(1) Å, Z = 16, and R = 0.057 for 2 024 independent reflections. The cobaltacyclopentane ring in the *cis* form has an ' opened-envelope ' conformation while that in the *trans* isomer is puckered. Although (2) and (3) are thermally more stable than the unsubstituted analogue, $[Co(\eta\text{-}C_5H_5)(C_4H_8)(PPh_3)]$ (4), their Co–C(α) distances are approximately equal to the reported values for (4) while the Co–P distances are distinctly longer.

In recent years it has become apparent that metallacyclic compounds play an important role in the transition-metal-catalyzed reactions of olefins and acetylenes. In earlier papers of this series we have described the formation of stable cobaltacyclopentadienes [equation (i)] and cobaltacyclopentenes [equation (ii)] from two molecules of acetylenes or by the combination of one molecule of acetylene and one molecule of olefin.[1,2] As a further extension of these reactions we aimed to prepare the saturated cobalt metallacycle by the reaction of two molecules of olefin.

In this paper we describe the finding that acrylonitrile forms cobaltacyclopentane derivatives according to equation (iii). We have also completed structural studies on the two isomeric dicyanocobaltacyclopentanes thus formed and our results are compared with the related unsubstituted cobaltacyclopentane (4) prepared by a Grignard reaction and its molecular structure determined by Diversi *et al.*[3] The thermal *cis* ⇌ *trans* isomerization, a feature of this novel metallacycle, has been described previously.[4]



Experimental

Preparation of Dicyanocobaltacyclopentane Complexes (2) *and* (3).—The reactions and column chromatography of (1) were carried out under an atmosphere of argon or nitrogen. Alumina (Sumitomo KCG-30) used for chromatography of (2) and (3) was activated by heating at 200 °C *in vacuo*. Commercially available acrylonitrile was used without further purification.

To a solution of $[Co(\eta\text{-}C_5H_5)(C_6H_6)(PPh_3)_2]$ [1] (1 g, 0.14 mmol) in benzene (20 cm³) was added acrylonitrile (4 cm³) and the dark red solution was stirred at room temperature for 1 h. After concentration the mixture was chromatographed on alumina. A dark red band of $[Co(\eta\text{-}C_5H_5)(CH_2CHCN)(PPh_3)]$ (1) was eluted with benzene–acrylonitrile (5 : 1) and the eluate was concentrated to *ca.* 5 cm³. To this solution, hydroquinone (100 mg), benzene (15 cm³), and acrylonitrile (5 cm³) were added and the mixture was heated at 100 °C in a sealed tube. After 48 h the solvent and the excess of acrylonitrile were evaporated and the residue was dissolved in a small amount of benzene. Chromatography on silica gel gave two dark red bands which were separated by elution with dichloromethane–tetrahydrofuran (thf) (40 : 1). From the first band the unreacted oily (1) (*ca.* 100 mg) was recovered. Concentration and addition of hexane to the second fraction gave dark red crystals (100 mg), a mixture of (2) and (3). Isomers (2) and (3) were separated by chromatography on activated alumina using CH_2Cl_2–thf (40 : 1) as eluant. The first fraction was concentrated and hexane added to give brown-red crystals of the *trans* isomer (3) (68 mg, 10%), m.p. 164 °C (decomp.) (Found: C, 71.3; H, 5.40; N, 5.75. Calc. for $C_{29}H_{26}CoN_2P$: C, 70.75; H, 5.30; N, 5.70%); δ ($CDCl_3$) 0.9—2.6 (m, 5 H), 4.0 (m, 1 H), and 4.68 (s, C_5H_5). The residue from the second fraction was treated with benzene–hexane (*ca.* 1 : 2) to give orange-red crystals of the *cis* isomer (2) solvated with one molecule of benzene (28 mg, 4%), m.p. 153 °C (decomp.) (Found: C, 73.2; H, 5.75; N, 5.05. Calc. for $C_{35}H_{32}CoN_2P$: C, 73.65; H, 5.65; N, 4.90%); δ ($CDCl_3$) 0.9—1.9 (m, 6 H) and 4.73 (s, C_5H_5).

† Part 9 is ref. 11.

‡ (1—5-η-Cyclopentadienyl)(1,4-dicyanobutane-1,4-diyl)(triphenylphosphine)cobalt.

Supplementary data available (No. SUP 23357, 26 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

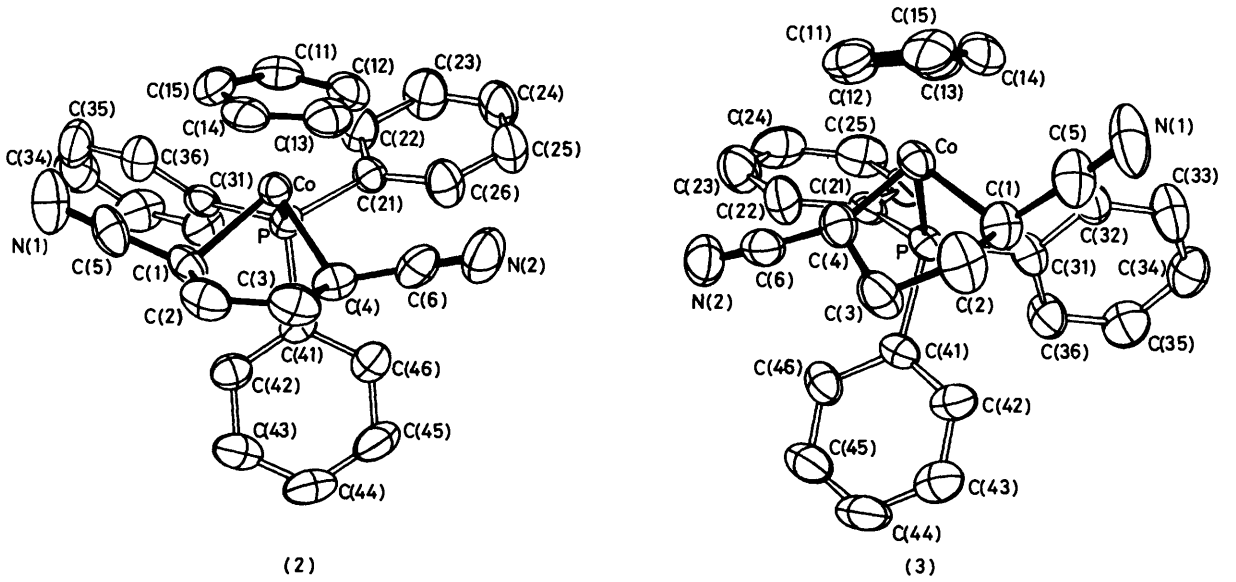


Figure. Molecular structures of complexes (2) and (3) with the atomic numbering schemes

X-*Ray Analysis*.—The crystal and refinement data are summarized in Table 1. *X*-Ray measurements were carried out with a Rigaku automatic four-circle diffractometer using a graphite monochromator.

Intensities were measured using ω—2θ scans and 10-s stationary background counts made at the lower and upper limits of each scan. A constant scan speed of 0.06° s^{-1} was used. Corrections were applied for Lorentz and polarization factors but not for absorption.

The structures were solved using three-dimensional Patterson and Fourier techniques and refined by block-diagonal least squares. The atomic scattering factors were from ref. 5. Anomalous-dispersion effects for Co were included in the calculation using Cromer's values of $\Delta f'$ and $\Delta f''$.[6] The absolute configuration of (3) was determined from 30 reflections with large Bijvoet differences. The hydrogens of the phenyl and the cyclopentadienyl rings were placed in calculated positions. The positions of metalla-ring hydrogens were revealed in the difference-Fourier maps. They were included in subsequent refinements with isotropic thermal parameters.

The solvent of crystallization in (2), C_6H_6, could not be resolved in the difference map; only three broad peaks were observed around (0.5, 0.5, 0.2) and these were assigned to three of the benzene carbons. No other chemically reasonable positions of other benzene atoms were indicated, despite the fact that the density, and elemental and n.m.r. analysis, best fitted the formula $C_{29}H_{26}CoN_2P\cdot C_6H_6$, leaving our model with a chemically incomplete solvent of crystallization in the large, otherwise vacant space.

Table 1. Crystal data

	(2)	(3)
Formula	$C_{29}H_{26}CoN_2P\cdot C_6H_6$	$C_{29}H_{26}CoN_2P$
M	570.6	492.5
Crystal size/mm	0.62 × 0.25 × 0.08	0.62 × 0.38 × 0.08
Space group (crystal system)	$P\bar{1}$ (triclinic)	*Fdd*2 (orthorhombic)
a/Å	11.464(3)	12.821(1)
b/Å	13.782(3)	65.833(20)
c/Å	9.277(2)	11.470(1)
α/°	87.48(2)	
β/°	110.23(1)	
γ/°	84.26(2)	
U/Å^3	1 363.6	9 681.2
Z	2	16
D_m(flotation)/g cm^{-3}	1.38(5)	1.34(5)
D_c/g cm^{-3}	1.390	1.352
F(000)	596	4 096
Radiation (λ/Å)	Mo-K_α (0.7107)	Cu-K_α (1.5406)
μ/cm^{-1}	7.4	69.4
No. of unique reflections	4 238	2 024
$[(\sin\theta)/\lambda]_{max.}$	0.65	0.63
R	0.067	0.057
R'	0.074	0.058
Maximum residual electron density (e Å^{-3})	0.78	0.62

Results and Discussion

Preparation of the Metallacycles.—Some disubstituted olefin (L) complexes of the type $[Co(\eta\text{-}C_5H_5)(PPh_3)L]$ have been prepared by the reaction of (cyclopentadienyl)bis(triphenylphosphine)cobalt with L (L = dimethyl maleate, dimethyl fumarate, fumaronitrile, or ethylene).[7,8] Similarly acrylonitrile reacts with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ in benzene at room temperature to give a dark red solution of $[Co(\eta\text{-}C_5H_5)(CH_2{=}CHCN)(PPh_3)]$ (1). Attempts to crystallize (1) have so far failed and its dark red oil gradually decomposes liberating free acrylonitrile. Complex (1) is stable only in the presence of excess of acrylonitrile. The n.m.r. spectrum of (1) in the presence of a small amount of acrylonitrile showed a singlet peak of C_5H_5 protons at 4.50 p.p.m. in C_6D_6, but we did not try further to characterize this complex.

On heating a benzene solution of (1) with free acrylonitrile and hydroquinone at 100 °C the olefin complex slowly decomposes forming brown precipitates. Work-up of the supernatant solution on column chromatography gave, beside unreacted (1), two stable complexes, (2) and (3), with empirical formula $Co(C_5H_5)(CH_2CHCN)_2(PPh_3)$. The ^1H n.m.r. spectra showed characteristic resonances of triphenylphosphine, a sharp singlet of cyclopentadienyl protons, and broad multiplets in the region of aliphatic protons whose integrated areas correspond to six protons.

Since the complexity of the n.m.r. spectra did not allow a

Table 2. Atomic parameters ($\times 10^4$) for complexes (2) and (3)

	(2)			(3)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Co	2 053(1)	1 951(1)	2 606(1)	4 435(1)	2 084(0)	−2 504(2)
P	2 712(1)	1 860(1)	5 139(2)	4 721(2)	1 815(0)	−3 640(2)
N(1)	242(7)	−291(5)	1 998(8)	5 251(10)	2 573(1)	−4 190(8)
N(2)	2 191(7)	4 709(4)	2 138(8)	5 092(7)	1 663(1)	−280(7)
C(1)	335(5)	1 551(5)	2 314(7)	5 724(7)	2 234(1)	−3 146(8)
C(2)	−609(6)	2 208(6)	946(7)	6 520(9)	2 264(1)	−2 188(10)
C(3)	−179(6)	3 212(5)	880(8)	6 554(8)	2 067(1)	−1 494(10)
C(4)	984(5)	3 257(4)	2 298(6)	5 439(7)	2 022(1)	−1 181(8)
C(5)	272(6)	523(5)	2 151(7)	5 479(10)	2 423(1)	−3 730(9)
C(6)	1 652(6)	4 071(4)	2 189(7)	5 271(7)	1 819(1)	−682(8)
C(11)	3 732(6)	1 200(5)	2 668(8)	3 349(7)	2 174(2)	−1 218(9)
C(12)	3 660(6)	2 175(5)	2 114(8)	2 919(7)	2 024(1)	−1 919(9)
C(13)	2 599(7)	2 358(5)	764(7)	2 876(8)	2 100(2)	−3 090(10)
C(14)	2 035(6)	1 498(5)	497(7)	3 331(9)	2 294(2)	−3 074(10)
C(15)	2 750(6)	785(4)	1 675(8)	3 612(9)	2 341(1)	−1 923(11)
C(21)	4 242(5)	2 306(4)	6 004(6)	3 670(6)	1 627(1)	−3 570(8)
C(22)	5 255(6)	1 721(4)	7 060(7)	3 441(7)	1 530(1)	−2 515(9)
C(23)	6 407(6)	2 091(5)	7 664(9)	2 598(7)	1 394(1)	−2 448(10)
C(24)	6 538(6)	3 019(5)	7 278(8)	2 004(7)	1 356(1)	−3 408(11)
C(25)	5 547(6)	3 602(5)	6 194(8)	2 233(7)	1 447(1)	−4 449(10)
C(26)	4 404(6)	3 243(5)	5 561(8)	3 054(7)	1 582(1)	−4 536(8)
C(31)	2 923(5)	650(4)	6 143(6)	4 803(7)	1 873(1)	−5 205(7)
C(32)	3 229(6)	548(4)	7 740(7)	4 508(8)	2 066(1)	−5 606(8)
C(33)	3 382(7)	−359(5)	8 492(8)	4 604(10)	2 111(1)	−6 793(9)
C(34)	3 251(7)	−1 173(5)	7 712(9)	4 949(8)	1 968(2)	−7 573(8)
C(35)	2 950(7)	−1 097(4)	6 145(9)	5 236(8)	1 775(1)	−7 162(9)
C(36)	2 800(6)	−180(4)	5 360(7)	5 173(7)	1 728(1)	−5 985(7)
C(41)	1 665(5)	2 543(4)	5 950(6)	5 939(6)	1 669(1)	−3 480(7)
C(42)	688(6)	2 096(4)	6 136(7)	6 834(7)	1 744(1)	−3 964(8)
C(43)	−216(6)	2 624(5)	6 563(8)	7 784(7)	1 647(2)	−3 875(10)
C(44)	−163(7)	3 587(5)	6 813(8)	7 826(8)	1 465(2)	−3 241(10)
C(45)	812(7)	4 028(5)	6 677(9)	6 937(8)	1 388(1)	−2 769(9)
C(46)	1 727(6)	3 515(4)	6 251(8)	6 014(7)	1 486(1)	−2 847(7)
C(51) *	698(1)	392(1)	296(2)			
C(52) *	623(2)	422(2)	128(3)			
C(53) *	532(2)	482(2)	87(2)			

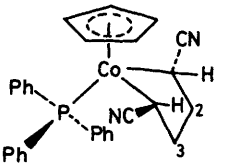
* Solvent of crystallization.

firm conclusion on the structures of (2) and (3), their crystals were subjected to *X*-ray crystallographic analysis.

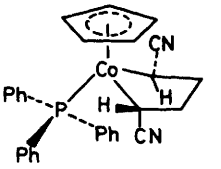
Crystal and Molecular Structures of (2) *and* (3).—The Figure shows a perspective view and the numbering scheme of complexes (2) and (3). The atomic co-ordinates are reported in Table 2 and important bond lengths and angles in Table 3.

The five-membered metallacycle system in the *cis* isomer (2) has an opened-envelope conformation first ' discovered ' by Churchill and Youngs [9] for a tantalacyclopentane complex. The C(1)–C(2)–C(3)–C(4) system is close to planar, the maximum deviation from the best plane being 0.035(9) Å. The dihedral angle between the C(1)–Co–C(4) system and the approximately planar C(1)–C(2)–C(3)–C(4) system is 47.5(3)°. The C(1)–C(2)–C(3)–C(4) plane is almost parallel to the cyclopentadienyl plane: the dihedral angle between them is only 0.5(3)° (Table 4).

Evidently, the opened-envelope conformation in (2) results from steric requirements. The cone angles of cyclopentadienyl and triphenylphosphine ligands are 136 and 145°, respectively,[10] leaving *ca.* 80° of cone-angle space at the Co atom available to the $(CH_2CHCN)_2$ unit. In (2) the two CN groups are oriented slightly upward towards the cyclopentadienyl ring from the C(1)–C(2)–C(3)–C(4) plane (see Figure) so as to minimize steric interaction with the cyclopentadienyl unit as well as with the triphenylphosphine. The other such conformation, *i.e.* type (I), is less favourable



(I)



(II)

because of increasing repulsion of the C(2)–C(3) unit by the triphenylphosphine and becomes possible only when a smaller phosphine, *e.g.* $PPhMe_2$ (cone angle 122°), is used instead of PPh_3.[4]

In contrast to the opened-envelope conformation of the metallacycle system in (2), that in the *trans* isomer (3) has the usual puckered conformation. This again can be ascribed to steric reasons. On changing the configuration of one of the α-carbons in (2) one obtains the conformation of type (II) for the *trans* isomer. This conformation has large steric repulsion between the triphenylphosphine and one of the CN groups which is directed toward the former. The only way to avoid this repulsion is to twist the C(2)–C(3) bond into the puckered conformation as in (3), leading the CN group at C(4) away from the triphenylphosphine.

Table 3. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

	(2)	(3)
(*a*) Bond lengths		
Co–P	2.199(2)	2.230(3)
Co–C(1)	2.029(6)	2.060(9)
Co–C(4)	2.024(6)	2.031(9)
Co–C(11)	2.073(7)	2.112(10)
Co–C(12)	2.093(8)	2.095(10)
Co–C(13)	2.086(8)	2.112(10)
Co–C(14)	2.073(7)	2.084(11)
Co–C(15)	2.075(7)	2.102(11)
P–C(21)	1.840(5)	1.840(5)
P–C(31)	1.827(5)	1.838(8)
P–C(41)	1.831(6)	1.842(8)
C(1)–C(2)	1.535(8)	1.513(15)
C(2)–C(3)	1.520(11)	1.523(14)
C(3)–C(4)	1.524(8)	1.503(13)
C(1)–C(5)	1.438(10)	1.452(13)
C(4)–C(6)	1.439(9)	1.471(12)
C(5)–N(1)	1.139(10)	1.155(13)
C(6)–N(2)	1.133(10)	1.147(12)
(*b*) Bond angles		
C(1)–Co–P	95.9(2)	92.2(3)
C(4)–Co–P	95.3(2)	100.0(3)
C(1)–Co–C(4)	77.5(3)	81.7(4)
Co–C(1)–C(2)	107.0(5)	110.2(7)
Co–C(4)–C(3)	106.5(4)	112.6(7)
C(1)–C(2)–C(3)	110.2(5)	106.6(8)
C(2)–C(3)–C(4)	108.5(5)	105.4(8)
Co–C(1)–C(5)	113.4(5)	113.7(7)
Co–C(4)–C(6)	112.7(5)	112.4(6)
(*c*) Torsion angles		
C(1)–C(2)–C(3)–C(4)	−5.6(7)	−51.9(10)
C(3)–C(2)–C(1)–C(5)	21.8(6)	−10.8(8)
C(2)–C(3)–C(4)–C(6)	−14.1(6)	−10.2(8)

Table 4. Important least-squares planes and atomic deviations (Å) therefrom for (2) and (3) *

(*a*) Complex (2)

Plane (A): C(1)–Co–C(4)

$$-0.1497X + 0.0537Y + 0.9794Z = 2.1596$$

[P 2.182(2), C(2) −1.033(11), C(3) −1.092(11)]

Plane (B): C(1)–C(2)–C(3)–C(4)

$$-0.7675X + 0.2601Y + 0.8011Z = 1.9955$$

[C(1) −0.015(9), C(2) 0.035(10), C(3) −0.033(10), C(4) 0.013(9), Co −1.166, P 0.104(17), C(5) −0.449 (12), C(6) −0.363(12), N(1) −0.828(15), N(2) −0.647(15)]

Plane (C): C(11)–C(12)–C(13)–C(14)–C(15)

$$-0.7729X + 0.2526Y + 0.7993Z = -0.9158$$

[Co 1.708(3), P 2.971(8), C(1) 2.874(10), C(2) 2.925(13), C(3) 2.845(13), C(4) 2.881(10), C(5) 2.452(14), C(6) 2.492(14), N(1) 2.081(17), N(2) 2.198(17)]

Interplanar angles (°):

A–B 47.5(3), A–C 47.8(3), B–C 0.5(3)

(*b*) Complex (3)

Plane (A): C(1)–Co–C(4)

$$-0.2880X + 0.8350Y + 0.4689Z = 8.4719$$

[P −2.196(4), C(2) 0.390(18), C(3) −0.333(17)]

Plane (B): Co–C(4)–C(3)

$$-0.1075X + 0.9334Y + 0.3423Z = 11.2128$$

[C(1) 0.489(24), C(2) 0.943(24), C(6) −1.030(22), N(2) −1.803(32)]

Plane (C): C(1)–C(2)–C(3)

$$-0.7184X + 0.3461Y + 0.6034Z = -2.3604$$

[Co 1.291(29), C(4) 1.141(23), C(5) 0.254(21), N(1) 0.487(31)]

Plane (D): C(11)–C(12)–C(13)–C(14)–C(15)

$$-0.9054X + 0.3918Y + 0.1635Z = 1.4832$$

[Co 1.726(5), P 2.965(13), C(1) 2.958(15), C(2) 3.623(19), C(3) 4.041(17), C(4) 2.803(14), C(5) 2.293(22), C(6) 3.039(18), N(1) 1.729(28), N(2) 3.157(23)]

Interplanar angles (°):

A–C 38.8(9), A–D 48.4(4), B–C 52.6(11)

* X, Y, and Z are co-ordinates (Å) along the crystallographic axis.

Puckering of the metallacyclic ring as in (3) has been reported for the unsubstituted analogue of (2) and (3), $[Co(\eta\text{-}C_5H_5)(C_4H_8)(PPh_3)]$, and related complexes of Rh and Ir.[3] It has been pointed out that one of the features of these metallacyclic systems is the presence of some C–C bonds significantly shorter than the standard $C(sp^3)$–$C(sp^3)$. In the present cyano-substituted cobalt metallacycles, however, no such trend is observed (Table 3).

The dicyano-substituted metallacyclic complexes (2) and (3) are much more stable than the unsubstituted analogue. In solution, (2) and (3) do not change at ambient temperature and begin to decompose only at elevated temperatures (100 °C), while the unsubstituted analogue (4) smoothly decomposes at room temperature.[11] However, the metal–carbon distances of the metallacycle in these three complexes are not significantly different within the limits of experimental error [Co–C(α) in (4): 2.027(5) and 2.021(5) Å], with the exception of the Co–C(1) distance for (3) which is *ca.* 0.03 Å larger. This is surprising since substantial shortening of the Co–C bond might be expected because of the strengthened σ bonding in (2) and (3). In fact it is well established that a metal–perfluoroalkyl bond of Fe, Co, or Ni is 0.06—0.07 Å shorter than an analogous metal–alkyl linkage, a dominant contribution to which is believed to be the high inductive effect of perfluoroalkyls.[12]

This feature of the Co–C(α) bonds in (2) and (3) is most probably associated with the greater bulk of the $(CH_2CHCN)_2$ unit than the $(CH_2CH_2)_2$ system in the unsubstituted metallacycle. The limited space at the Co might not allow the bulky $(CH_2CHCN)_2$ system to approach too closely. In this connection, the Co–P distances are noteworthy. The metal–phosphine bond of the unsubstituted cobaltacyclopentane is reported to be 2.146(1) Å, while those in (2) and (3) are 2.199(2) and 2.230(3) Å, respectively. The value is the largest in the *trans* isomer (3) where one of the CN groups is oriented relatively close to the triphenylphosphine and the steric repulsion is expected to be the largest.

It is now well established that, in the thermal decomposition of cobalt metallocycles of the type $[Co(\eta\text{-}C_5H_5)(PPh_3)]$, dissociation of the co-ordinated phosphine is a prerequisite for Co–C bond splitting.[11] Consequently, the Co–P bond strength, as well as the strength of the Co–C(α) bond, is an essential factor in determining the thermal stability. The fact that the dicyano-substituted metallacycles have distinctly longer Co–P bond lengths than the thermally much less stable unsubstituted analogue and that the Co–C(α) distances are approximately equal in the three metallacycles lead us to conclude that the metal–ligand bond length observed in the crystals cannot be related with its thermal stability, especially in a crowded complex.

References

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