Cobalt Metallacycles. Part 16.[1] *X*-Ray Structures of 4-Iminocobaltacyclobutene Complexes†

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Three 4-iminocobaltacyclobutene complexes, $[\mathrm{Co\{C(R^1){=}C(R^2)C({=}NC_6H_4Me\text{-}}p)\}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})]$ have been analysed by single-crystal *X*-ray analyses. Crystals of (**1**) ($\mathrm{R^1}$ = Ph, $\mathrm{R^2} = \mathrm{CO_2Me}$; $\mathrm{CH_2Cl_2}$ solvate) are triclinic, space group $P\bar{1}$, with a = 12.381(3), b = 13.987(4), c = 11.209(4) Å, α = 91.16(3), β = 103.30(2), γ = 77.14(2)°, Z = 2, and R = 0.066 for 3 055 reflections. Crystals of (**2**) ($\mathrm{R^1}$ = Me, $\mathrm{R^2} = \mathrm{CO_2Me}$) are monoclinic, space group $P2_1/c$, with a = 12.062(5), b = 14.945(4), c = 17.817(5) Å, β = 113.70(4)°, Z = 4, and R = 0.052 for 2 842 reflections. Crystals of (**3**) ($\mathrm{R^1} = \mathrm{CO_2Me}$, $\mathrm{R^2}$ = Ph) are triclinic, space group $P\bar{1}$, with a = 12.271(6), b = 13.216(5), c = 10.833(4) Å, α = 96.07(3), β = 98.77(4), γ = 102.23(3)°, Z = 2, and R = 0.048 for 4 324 reflections. The Co–C($\mathrm{R^1}$) distance in these complexes depends on the bulkiness of the substituent $\mathrm{R^1}$, varying from 1.966(8) Å for $\mathrm{R^1}$ = Ph (**1**), to 1.931(5) Å for $\mathrm{R^1} = \mathrm{CO_2Me}$ (**3**), and to 1.908(7) Å for $\mathrm{R^1}$ = Me (**2**). In all cases the substituent of the imino group, $\mathrm{C_6H_4Me}$-*p*, is located *syn* with respect to the metal. Treatment of (**1**) with methyl iodide gives a cationic complex which has been isolated as $[\mathrm{Co\{C(Ph){=}C(CO_2Me)C(NMeC_6H_4Me\text{-}}p)\}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})]\mathrm{PF_6}$ (**4**). Crystals of (**4**) are triclinic, space group $P\bar{1}$, with a = 13.658(3), b = 14.142(2), c = 10.517(3) Å, α = 94.42(2), β = 95.39(1), γ = 102.62(1)°, Z = 2, and R = 0.082 for 2 314 reflections. The methyl group originating from methyl iodide is bound to the imino nitrogen. Metallacyclobutadiene character in (**4**) is apparent from the shorter metal–carbon bonds and more averaged C–C distances than in the parent complex (**1**).

The preceding paper[1] described the formation of four-membered cobalt metallacycles by the oxidative cyclization of alkyne and isocyanide units with (η^5-cyclopentadienyl)cobalt. When unsymmetrical acetylenes were employed the reaction was highly regiospecific, giving only one of the two possible isomers. Two such complexes derived from $\mathrm{PhC_2CO_2Me}$ and $\mathrm{MeC_2CO_2Me}$ have molecular formula $[\mathrm{Co\{C(R^1){=}C(R^2)C({=}NC_6H_4Me\text{-}}p)\}(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})]$(**1**; $\mathrm{R^1}$ = Ph, $\mathrm{R^2} = \mathrm{CO_2Me}$; **2**; $\mathrm{R^1}$ = Me, $\mathrm{R^2} = \mathrm{CO_2Me}$). On heating a benzene solution (**1**), it isomerizes to complex (**3**) ($\mathrm{R^1} = \mathrm{CO_2Me}$, $\mathrm{R^2}$ = Ph).

In this paper we have determined the positions of the substituents as well as the 4-iminocobaltacyclobutene framework of complexes (**1**)—(**3**). It was also shown in the preceding paper that facile addition of methyl iodide to (**1**) gives the formal metallacyclobutadiene cationic complex $[\mathrm{Co\{C(Ph){=}C(CO_2Me)C(NMeC_6H_4Me\text{-}}p)(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})]\text{-}\mathrm{PF_6}$ (**4**). To check the structural change in the metallacycle, (**4**) has also been analysed by *X*-ray crystallography and reported herein.

Formation of four-membered metallacycles by the reaction of a carbene or a carbyne complex with an alkyne is known. Some products of such reactions, titanacyclobutenes[2] and tungstenacyclobutadienes,[3] have been characterized by *X*-ray structural analyses.

Experimental

The crystal and refinement data are summarized in Table 1. *X*-Ray measurements were carried out with a Rigaku automatic four-circle diffractometer 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° $\mathrm{s^{-1}}$ was used. Lorentz and polarization corrections were applied.

The structures were solved using three-dimensional Patterson and Fourier techniques and refined by block-diagonal least squares. The Co atom in each case was located from a Patterson map. For each complex a subsequent difference-Fourier synthesis revealed the positions of all the non-hydrogen atoms. The hydrogen atoms of the phenyl and cyclopentadienyl rings were placed in calculated positions and included in subsequent refinements with isotropic thermal parameters. Methyl protons in (**3**) could be located from a difference Fourier map. In the final stage of refinements, weights were applied for (**1**) and (**4**), according to the scheme $w = 1.0/\sigma(F_o)$ where $|F_o| \geqslant 70.0$ for (**1**) and $|F_o| \geqslant 40.0$ for (**4**). The standard deviation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}$, where m and n are numbers of reflections and refined parameters respectively, was 3.64, 5.01, 1.47, and 5.78 for (**1**)—(**4**), respectively. Anomalous dispersion effects for Co were included in the calculation using Δf and $\Delta f''$ values of ref. 4. Atomic scattering factors were from International Tables.[5]

Elemental analysis and spectral data showed crystals of (**4**) to have 0.125 molecule of $\mathrm{CH_2Cl_2}$ per molecular unit as solvent of crystallization. This could not be resolved in the difference map; only broad peaks were observed around (0.0, 0.5, 0.5) with a maximum electron density of 1.4 e $\mathrm{Å^{-3}}$. Attempts to resolve the $\mathrm{CH_2Cl_2}$ molecule by assuming space group $P1$ instead of $P\bar{1}$ were not successful. Thus in the refinement of (**4**) we did not include these peaks which were attributed to highly disordered solvent of crystallization in the large, otherwise vacant space.

Results and Discussion

Molecular Structures of (**1**), (**2**), *and* (**3**).—Figures 1 and 2 show the perspective views and numbering schemes of complexes (**1**), (**2**), and (**3**). The atomic co-ordinates are reported

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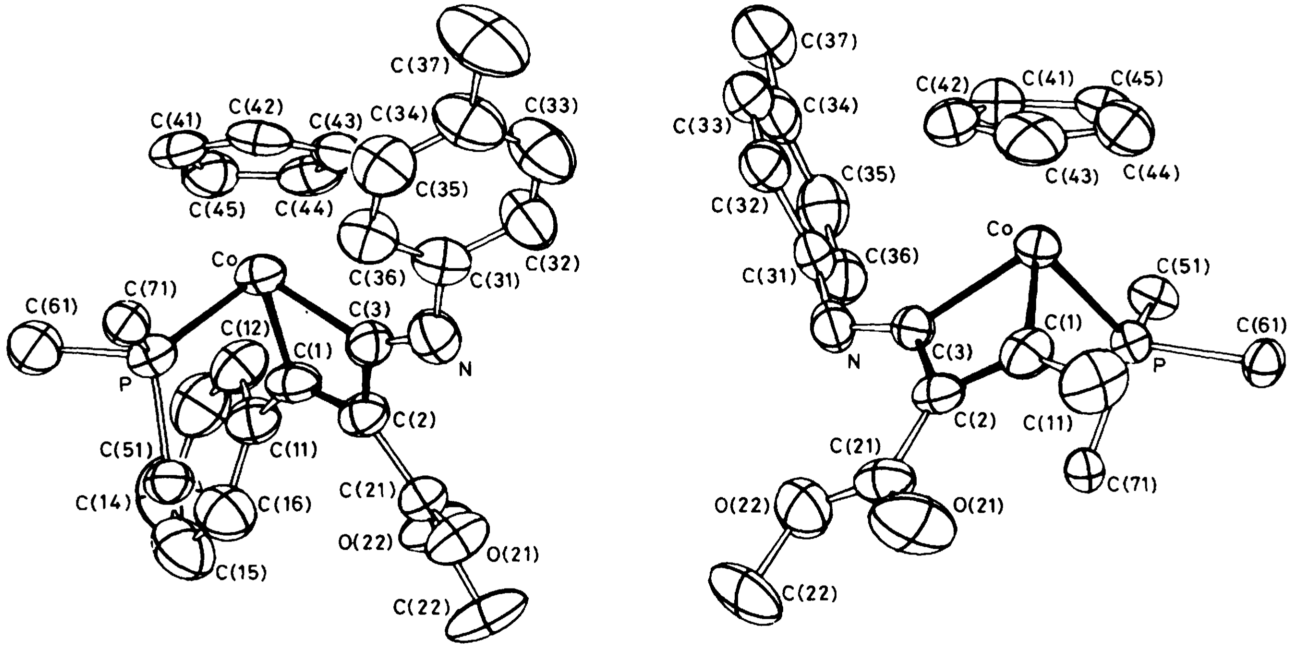
† *Supplementary data available* (No. SUP 56490, 14 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Crystal data

Complex	**(1)**	**(2)**	**(3)**	**(4)**
Formula	$C_{41}H_{35}CoNO_2P\cdot CH_2Cl_2$	$C_{36}H_{33}CoNO_2P$	$C_{41}H_{35}CoNO_2P$	$C_{42}H_{38}CoF_6NO_2P_2$
M	748.5	601.5	663.6	823.6
Crystal size/mm	0.30 × 0.26 × 0.10	0.16 × 0.30 × 0.50	0.30 × 0.25 × 0.10	0.37 × 0.26 × 0.10
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
a/Å	12.381(3)	12.062(5)	12.271(6)	13.658(3)
b/Å	13.987(4)	14.945(4)	13.216(5)	14.142(2)
c/Å	11.209(4)	17.817(5)	10.833(4)	10.517(3)
α/°	91.16(3)		96.07(3)	94.42(2)
β/°	103.30(2)	113.70(4)	98.77(4)	95.39(1)
γ/°	77.14(2)		102.23(3)	102.62(1)
U/Å^3	1 840.8	2 940.8	1 679.4	1 963.5
Z	2	4	2	2
D_m (flotation)/g cm^{-3}	1.34(5)	1.35(5)	1.31(5)	1.38(5)
D_c/g cm^{-3}	1.350	1.359	1.312	1.393
F(000)	776	1 256	692	848
Radiation (λ/Å)	Mo-K_α (0.7107)	Mo-K_α (0.7107)	Mo-K_α (0.7107)	Mo-K_α (0.7107)
μ/cm^{-1}	7.1	7.0	5.9	6.1
No. of unique reflections	3 055	2 842	4 324	2 314
$[(\sin\theta)/\lambda]_{max.}$	0.59	0.65	0.65	0.54
R	0.066	0.052	0.048	0.082
R'	0.076	0.057	0.049	0.105
Maximum residual electron density (e Å^{-3})	0.43	0.46	0.37	1.44



(1) (2)

Figure 1. Molecular structures of complexes (**1**) and (**2**) with atomic numbering schemes. The three phenyl rings of the phosphine have been omitted with only the first atoms C(51), C(61), and C(71) being shown

in Table 2, where C(80), Cl(1), and Cl(2) denote a solvent of crystallization (CH_2Cl_2) for complex (**1**). Important bond lengths and angles are listed in Table 3.

As shown in Table 4, the four-membered metallacycles have good planarity forming dihedral angles with the η^5-C_5H_5 ring of 46.3(3), 44.1(3), and 43.8(2)° for (**1**)—(**3**) respectively. In each case, the imino-plane, C(3)–N–C(31) is almost coplanar with the metallaring, dihedral angles being 10.4(5) (**1**), 5.4(5) (**2**), and 8.6(3)° (**3**). The *p*-tolyl group is oriented *syn* with respect to the metal towards the bulky triphenylphosphine ligand. An *anti* configuration of the imino group would have afforded the *p*-tolyl group more space and this has been demonstrated by the room temperature isomerization of the imino group geometry in (**4**).[1] An explanation for the formation of the sterically crowded *syn* product is given in the preceding paper.[1]

By comparing the bond lengths in (**1**), (**2**), and (**3**) (Table 3),

Table 2. Atomic co-ordinates (× 10^4) for complexes (**1**), (**2**), (**3**), and (**4**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) Complex (**1**)							
Co	992(1)	2 329(1)	4 592(1)	C(43)	387(8)	2 096(7)	6 125(8)
P	1 778(2)	1 634(2)	3 114(2)	C(44)	−354(7)	2 914(6)	5 415(9)
C(1)	1 282(7)	3 603(5)	4 221(8)	C(45)	−805(7)	2 584(7)	4 260(8)
C(2)	2 284(7)	3 511(5)	5 031(8)	C(51)	2 860(7)	2 185(6)	2 690(8)
C(3)	2 432(6)	2 534(6)	5 652(7)	C(52)	2 684(8)	2 622(7)	1 534(8)
N	3 149(6)	2 222(5)	6 619(6)	C(53)	3 503(9)	3 083(7)	1 283(10)
C(11)	661(7)	4 396(6)	3 324(8)	C(54)	4 470(9)	3 063(7)	2 139(10)
C(12)	−471(7)	4 805(6)	3 233(8)	C(55)	4 692(9)	2 625(8)	3 297(9)
C(13)	−1 036(9)	5 557(7)	2 663(10)	C(56)	3 858(8)	2 178(6)	3 536(9)
C(14)	−493(10)	5 865(8)	1 538(10)	C(61)	738(8)	1 684(6)	1 633(8)
C(15)	634(11)	5 432(8)	1 634(9)	C(62)	931(10)	1 016(7)	716(9)
C(16)	1 230(9)	4 710(7)	2 520(9)	C(63)	154(12)	1 140(9)	−424(10)
C(21)	3 130(7)	4 134(6)	5 283(8)	C(64)	−787(11)	1 923(9)	−646(10)
O(21)	4 137(5)	3 837(4)	5 655(6)	C(65)	−960(10)	2 573(9)	272(10)
C(22)	3 431(9)	5 750(7)	5 162(12)	C(66)	−218(8)	2 479(8)	1 395(9)
O(22)	2 637(5)	5 085(4)	5 050(6)	C(71)	2 465(7)	323(5)	3 306(7)
C(31)	3 173(7)	1 340(6)	7 264(8)	C(72)	3 522(8)	−72(6)	3 126(9)
C(32)	3 301(9)	1 383(7)	8 507(9)	C(73)	4 021(8)	−1 077(7)	3 301(10)
C(33)	3 386(10)	549(8)	9 193(10)	C(74)	3 408(8)	−1 702(6)	3 615(9)
C(34)	3 366(10)	−350(7)	8 654(10)	C(75)	2 320(8)	−1 335(7)	3 760(9)
C(35)	3 285(9)	−391(7)	7 403(10)	C(76)	1 847(7)	−332(6)	3 605(8)
C(36)	3 178(8)	444(7)	6 688(9)	C(80)	5 122(13)	3 616(10)	8 529(15)
C(37)	3 426(13)	−1 297(9)	9 420(12)	Cl(1)	6 270(4)	4 070(4)	8 262(5)
C(41)	−359(7)	1 572(6)	4 265(8)	Cl(2)	3 990(4)	4 692(4)	8 621(4)
C(42)	401(7)	1 261(6)	5 418(8)				
(*b*) Complex (**2**)							
Co	8 081(1)	4 505(1)	1 113(1)	C(44)	9 167(7)	5 591(5)	1 027(5)
P	9 192(1)	3 429(1)	1 879(1)	C(45)	9 094(6)	5 616(4)	1 792(5)
O(21)	5 979(6)	2 514(4)	−1 039(3)	C(51)	9 698(5)	3 569(4)	2 995(4)
O(22)	4 895(4)	2 505(4)	−287(3)	C(52)	9 081(6)	4 138(5)	3 301(4)
N	5 664(4)	3 832(4)	1 087(3)	C(53)	9 417(7)	4 196(6)	4 143(5)
C(1)	7 677(6)	3 758(4)	171(4)	C(54)	10 354(8)	3 679(6)	4 677(4)
C(2)	6 622(6)	3 418(4)	150(4)	C(55)	10 951(7)	3 106(5)	4 372(4)
C(3)	6 533(5)	3 853(4)	862(3)	C(56)	10 648(6)	3 048(5)	3 540(4)
C(11)	8 301(8)	3 624(5)	−412(5)	C(61)	10 651(5)	3 232(4)	1 802(4)
C(21)	5 817(6)	2 773(4)	−454(4)	C(62)	11 377(6)	3 973(4)	1 838(5)
C(22)	4 052(8)	1 877(6)	−872(6)	C(63)	12 505(6)	3 867(5)	1 818(5)
C(31)	5 659(5)	4 323(4)	1 762(4)	C(64)	12 928(6)	3 031(5)	1 755(4)
C(32)	5 162(6)	5 181(4)	1 660(4)	C(65)	12 232(6)	2 298(5)	1 726(4)
C(33)	5 170(6)	5 657(5)	2 332(4)	C(66)	11 102(5)	2 394(4)	1 752(4)
C(34)	5 636(6)	5 298(5)	3 120(4)	C(71)	8 509(5)	2 311(4)	1 728(4)
C(35)	6 066(6)	4 425(5)	3 199(4)	C(72)	8 375(6)	1 802(4)	1 028(4)
C(36)	6 071(6)	3 938(5)	2 538(4)	C(73)	7 865(7)	957(5)	918(5)
C(37)	5 693(7)	5 833(5)	3 864(5)	C(74)	7 449(6)	621(5)	1 476(5)
C(41)	7 867(6)	5 712(4)	1 667(5)	C(75)	7 564(6)	1 121(5)	2 158(5)
C(42)	7 173(6)	5 733(4)	812(5)	C(76)	8 081(5)	1 956(4)	2 279(4)
C(43)	7 980(8)	5 660(5)	427(5)				
(*c*) Complex (**3**)							
Co	3 544(0)	2 331(0)	4 031(1)	C(41)	3 721(5)	1 562(4)	5 637(4)
P	2 256(1)	1 425(1)	2 452(1)	C(42)	4 545(4)	2 526(4)	5 825(4)
O(11)	5 872(3)	946(3)	3 957(3)	C(43)	3 974(4)	3 333(4)	5 763(4)
O(12)	5 135(3)	766(2)	1 897(3)	C(44)	2 799(4)	2 883(4)	5 503(4)
N	3 859(3)	4 344(3)	2 827(3)	C(45)	2 654(4)	1 790(4)	5 431(4)
C(1)	4 786(3)	2 131(3)	3 205(4)	C(51)	2 125(4)	1 866(3)	905(4)
C(2)	5 024(3)	3 054(3)	2 774(4)	C(52)	1 119(4)	2 041(4)	300(4)
C(3)	4 083(3)	3 500(3)	3 107(4)	C(53)	1 046(5)	2 418(4)	−852(5)
C(11)	5 338(3)	1 240(3)	3 099(4)	C(54)	1 975(5)	2 607(4)	−1 420(5)
C(12)	5 539(5)	−180(4)	1 675(5)	C(55)	2 977(5)	2 417(4)	−856(4)
C(21)	5 939(3)	3 510(3)	2 108(4)	C(56)	3 064(4)	2 044(4)	294(4)
C(22)	6 977(3)	3 222(3)	2 282(4)	C(61)	809(3)	1 268(3)	2 780(4)
C(23)	7 823(4)	3 630(4)	1 648(5)	C(62)	53(4)	307(4)	2 603(5)
C(24)	7 664(4)	4 320(4)	819(5)	C(63)	−1 026(4)	219(4)	2 893(6)
C(25)	6 637(4)	4 607(4)	622(5)	C(64)	−1 349(4)	1 085(5)	3 373(5)
C(26)	5 794(4)	4 223(4)	1 275(5)	C(65)	−611(4)	2 055(4)	3 525(5)
C(31)	2 897(4)	4 704(3)	3 070(4)	C(66)	461(4)	2 149(3)	3 231(4)
C(32)	2 865(4)	5 278(4)	4 198(5)	C(71)	2 364(3)	67(3)	2 082(4)
C(33)	1 931(5)	5 676(5)	4 347(5)	C(72)	2 169(5)	−439(4)	860(5)

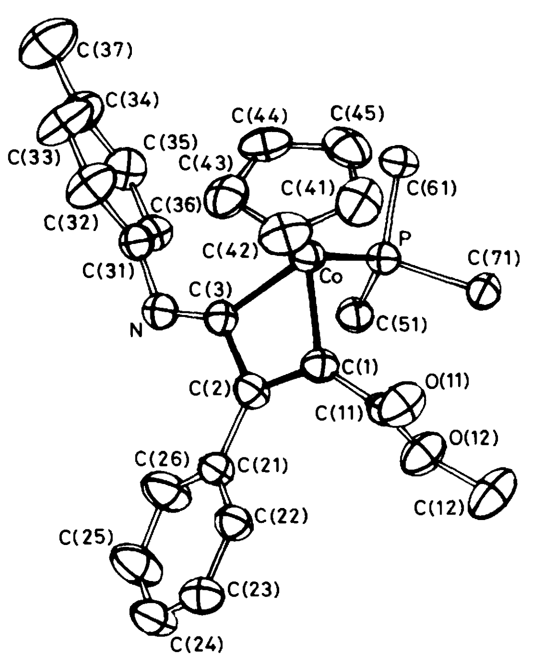
Table 2 (*continued*)

Atom	x	y	z	Atom	x	y	z
(*c*) Complex (**3**)							
C(34)	1 005(4)	5 537(4)	3 384(5)	C(73)	2 234(6)	−1 482(5)	645(6)
C(35)	1 047(4)	4 970(4)	2 257(4)	C(74)	2 485(6)	−2 020(4)	1 627(7)
C(36)	1 983(4)	4 560(3)	2 096(4)	C(75)	2 665(6)	−1 522(4)	2 831(6)
C(37)	2(5)	6 009(5)	3 555(6)	C(76)	2 625(5)	−489(4)	3 065(5)
(*d*) Complex (**4**)							
Co	2 314(1)	2 071(1)	1 924(1)	C(44)	1 375(9)	1 731(9)	3 342(10)
P	3 372(3)	3 230(2)	1 104(3)	C(45)	1 990(10)	1 077(9)	3 266(11)
C(1)	1 210(8)	2 105(8)	642(10)	C(51)	4 652(10)	3 053(9)	1 037(12)
C(2)	1 291(9)	1 319(8)	−154(11)	C(52)	5 142(10)	2 823(11)	2 111(15)
C(3)	2 112(9)	1 014(8)	552(11)	C(53)	6 153(11)	2 670(11)	2 114(17)
C(11)	503(9)	2 733(8)	407(12)	C(54)	6 594(12)	2 707(11)	971(19)
C(12)	53(10)	3 113(9)	1 426(13)	C(55)	6 084(12)	2 912(12)	−47(17)
C(13)	−634(10)	3 678(10)	1 192(14)	C(56)	5 127(11)	3 098(10)	−44(13)
C(14)	−871(12)	3 912(12)	−27(16)	C(61)	3 017(9)	3 499(9)	−519(11)
C(15)	−412(11)	3 557(11)	−1 006(14)	C(62)	2 868(9)	2 773(9)	−1 527(11)
C(16)	261(10)	2 962(9)	−814(12)	C(63)	2 609(11)	2 957(10)	−2 784(12)
C(21)	630(10)	912(8)	−1 398(11)	C(64)	2 500(12)	3 891(11)	−3 029(13)
C(22)	665(14)	602(12)	−3 652(12)	C(65)	2 631(11)	4 604(10)	−2 017(15)
O(21)	−264(7)	613(7)	−1 525(9)	C(66)	2 897(10)	4 436(9)	−783(12)
O(22)	1 214(7)	919(6)	−2 353(8)	C(71)	3 558(9)	4 410(8)	2 064(11)
N	2 397(8)	199(7)	358(9)	C(72)	2 703(10)	4 747(9)	2 349(12)
C(30)	1 860(11)	−594(9)	−655(13)	C(73)	2 804(11)	5 588(10)	3 092(15)
C(31)	3 204(11)	−25(9)	1 160(11)	C(74)	3 764(14)	6 151(10)	3 606(15)
C(32)	2 950(10)	−753(10)	1 961(13)	C(75)	4 601(11)	5 824(10)	3 364(14)
C(33)	3 719(12)	−1 016(10)	2 740(15)	C(76)	4 482(10)	4 962(10)	2 560(13)
C(34)	4 715(13)	−546(10)	2 726(14)	P(2)	8 373(4)	2 040(4)	4 715(4)
C(35)	4 937(11)	176(11)	1 921(16)	F(1)	8 357(10)	2 987(10)	4 019(16)
C(36)	4 185(11)	445(10)	1 115(13)	F(2)	8 336(11)	1 102(9)	5 409(12)
C(37)	5 602(15)	−808(13)	3 556(20)	F(3)	8 363(15)	2 545(13)	6 026(13)
C(41)	2 999(9)	1 596(9)	3 553(11)	F(4)	8 253(24)	1 538(15)	3 394(14)
C(42)	2 981(10)	2 575(9)	3 834(10)	F(5)	7 207(11)	1 808(14)	4 633(17)
C(43)	1 981(10)	2 670(9)	3 669(10)	F(6)	9 509(10)	2 290(14)	4 818(18)

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

	(**1**)	(**2**)	(**3**)	(**4**)
Co–P	2.211(3)	2.185(2)	2.190(2)	2.221(4)
Co–C(1)	1.966(8)	1.908(7)	1.931(5)	1.937(11)
Co–C(2)	2.513(9)	2.500(6)	2.521(4)	2.506(10)
Co–C(3)	1.978(8)	1.991(6)	1.980(4)	1.950(11)
Co–C(41)	2.132(9)	2.121(7)	2.112(5)	2.101(13)
Co–C(42)	2.116(10)	2.095(7)	2.094(5)	2.127(11)
Co–C(43)	2.085(10)	2.091(8)	2.105(4)	2.093(12)
Co–C(44)	2.091(9)	2.130(8)	2.096(5)	2.074(12)
Co–C(45)	2.119(9)	2.127(7)	2.101(5)	2.078(13)
C(1)–C(2)	1.340(11)	1.357(10)	1.342(6)	1.369(16)
C(2)–C(3)	1.501(11)	1.468(10)	1.477(6)	1.450(17)
C(1)–C(11)	1.463(10)	1.520(13)	1.480(6)	1.467(18)
C(2)–C(21)	1.482(13)	1.480(8)	1.483(6)	1.515(15)
C(3)–N	1.248(9)	1.263(9)	1.260(6)	1.302(16)
P–C(51)	1.839(10)	1.841(6)	1.827(4)	1.826(14)
P–C(61)	1.843(9)	1.844(7)	1.837(4)	1.822(13)
P–C(71)	1.836(7)	1.835(6)	1.833(4)	1.838(11)
C(1)–Co–C(3)	68.6(3)	68.4(3)	67.3(2)	68.1(5)
Co–C(1)–C(2)	97.2(5)	98.5(5)	99.2(3)	97.1(8)
Co–C(3)–C(2)	91.5(4)	91.3(4)	92.5(3)	93.8(8)
C(1)–C(2)–C(3)	102.8(7)	101.8(5)	100.5(4)	101.0(9)
Co–C(3)–N	142.0(8)	139.8(5)	140.9(4)	137.2(9)

the most striking difference is observed in the distances between Co and C(1), apparently a function of the bulkiness of the substituent R^1. Complex (**1**) with the bulky phenyl group at C(1) has the longest Co–C(1) bond [1.966(8) Å], (**2**) with the methyl group has the shortest [1.908(7) Å], and (**3**) with the



(**3**)

Figure 2. Molecular structure of complex (**3**) with atomic numbering scheme. The three phenyl rings of the phosphine have been omitted with only the first atoms C(51), C(61), and C(71) being shown

Table 4. Important least-squares planes and atomic deviations (Å)*

(*a*) Complex (**1**)

Plane A: Co, C(1), C(2), C(3)
$0.5812x - 0.3126y - 0.8055z = -4.4501$
[Co 0.000(0), C(1) −0.013(5), C(2) 0.016(6), C(3) −0.011(4), C(11) 0.003(17), C(21) 0.125(13), N −0.231(15), C(31) −0.411(20)]

Plane B: C(41), C(42), C(43), C(44), C(45)
$-0.9257x - 0.3698y + 0.5373z = 2.1583$
[Co −1.735(4), P −3.165(9), C(1) −2.949(12), C(2) −3.562(13), C(3) −2.853(12)]

Plane C: C(3), N, C(31)
$0.6467x - 0.3869y - 0.6858z = -3.7687$

Interplane angles (°): A—B 46.3(3), A—C 10.4(5)

(*b*) Complex (**2**)

Plane A: Co, C(1), C(2), C(3)
$-0.2943x + 0.7569y - 0.4160z = 1.4022$
[Co 0.000(0), C(1) −0.003(4), C(2) 0.003(5), C(3) −0.002(3), C(11) 0.056(15), C(21) 0.006(11), N 0.117(12), C(31) 0.173(16)]

Plane B: C(41), C(42), C(43), C(44), C(45)
$0.0949x + 0.9954y - 0.0271z = 9.3138$
[Co 1.741(4), P 3.251(8), C(1) 2.852(11), C(2) 3.478(12), C(3) 2.875(11)]

Plane C: C(3), N, C(31)
$-0.2028x + 0.7712y - 0.4710z = 2.1199$

Interplane angles (°) A—B 44.1(3), A—C 5.4(5)

(*c*) Complex (**3**)

Plane A: Co, C(1), C(2), C(3)
$0.4261x + 0.2496y + 0.7029z = 5.6904$
[Co 0.001(0), C(1) −0.045(2), C(2) 0.056(3), C(3) −0.036(2), C(11) −0.130(8), C(21) 0.177(6), N −0.087(7), C(31) −0.286(10)]

Plane B: C(41), C(42), C(43), C(44), C(45)
$-0.1722x - 0.0349y + 0.9975z = 5.2260$
[Co −1.727(3), P −3.118(6), C(1) −2.873(7), C(2) −3.431(7), C(3) −2.893(7)]

Plane C: C(3), N, C(31)
$0.2874x + 0.2823y + 0.7782z = 5.3650$

Interplane angles (°) A—B 43.8(2), A—C 8.6(3)

(*d*) Complex (**4**)

Plane A: Co, C(1), C(2), C(3)
$-0.5772x - 0.4996y + 0.6194z = -2.0345$
[Co 0.000(0), C(1) 0.012(6), C(2) −0.016(8), C(3) 0.013(6), C(11) −0.028(24), C(21) −0.017(20), N 0.238(22), C(30) 0.561(29), C(31) 0.282(30)]

Plane B: C(41), C(42), C(43), C(44), C(45)
$-0.1232x - 0.1951y + 0.9911z = 2.7690$
[Co −1.725(6), P −3.077(14), C(1) −2.884(17), C(2) −3.511(18), C(3) −2.829(18)]

Plane C: C(3), N, C(30), C(31)
$0.6221x + 0.3150y - 0.7307z = 1.8316$
[C(3) −0.009(4), N 0.019(8), C(30) −0.012(5), C(31) −0.012(5)]

Interplane angles (°): A—B 45.1(5), A—C 12.8(6)

* x, y, and z are co-ordinates (Å) along the crystallographic axis.

intermediate size CO_2Me group has an intermediate bond length [1.931(5) Å]. We have noted previously that metal–carbon bond lengths are determined primarily by the bulk of substituents at the carbon atom.[6] Also, the Co–P distance of 2.211(3) Å in (**1**) is clearly the largest of the three [*cf.* 2.185(2) Å in (**2**) and 2.190(2) Å in (**3**)].

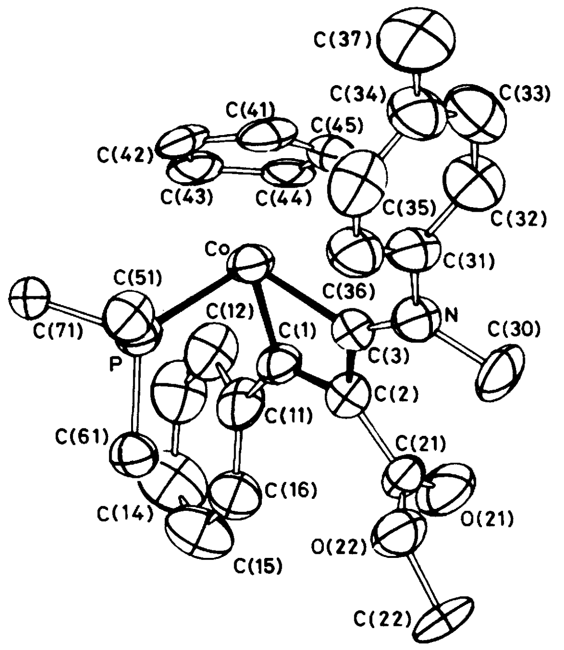
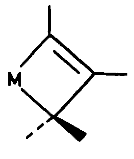


Figure 3. Molecular structure of complex (**4**) with atomic numbering scheme. The three phenyl rings of the phosphine have been omitted with only the first atoms C(51), C(61), and C(71) being shown

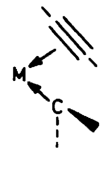
The structural parameters of these 4-iminocobaltacyclobutene frameworks may be compared with those of titanacyclobutenes reported by Tebbe and co-workers.[2]

The shorter metal–C(σ) bond in the former (1.908—1.991 Å) than in the latter (2.050—2.122 Å) is in accord with the general tendency that for the first-row transition metals the metal–C(σ) bond becomes shorter as the atomic number of the metal increases.[7] Structural results of the trimethylsilyl-substituted titanacyclobutenes have indicated a substantial contribution of a valence isomer (**B**) in addition to the metallacyclobutene formalism (**A**). Structural data of the 4-iminocobaltacyclobutenes (**1**)—(**3**) are consistent with the metallacyclobutene form (**A**): no contribution of a valence isomer (**C**) was indicated. To realize form (**C**) either disssociation of the phosphine ligand or slippage of η^5-C_5H_5 ligand to η^3-C_5H_5 is necessary, both of which would require high energy. The isomerization of (**1**) to (**3**) *via* (**C**) has been observed only at an elevated temperature.[1]

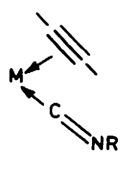
Molecular Structure of (**4**).—The atom-numbering scheme is shown in Figure 3. The methyl group [C(30)] originating from methyl iodide is bonded to nitrogen in an *anti* position with respect to the metal. C(3)–N–C(31)–C(30) is planar and almost in the same plane as that of the metallacycle [Table 4, dihedral angle 12.8(6)°]. The cationic charge brought about by addition of CH_3^+ to the nitrogen is expected to be delocalized into the metallacycle system to some extent. Although the structure determination of (**4**) was less accurate than that of (**1**) (see Experimental section), it was interesting to compare their structural differences. As shown in Table 3, the C(3)–N bond length in (**4**) is 0.05 Å longer than that in (**1**). The Co–C(1) bond



(**A**)



(**B**)



(**C**)

in (**4**) [1.937(11) Å] is shorter than in (**1**) [1.966(8) Å]. Also, the C(1)–C(2) bond appears to be elongated while the C(2)–C(3) bond is shorter in (**4**) than in (**1**). All these tendencies indicate delocalization of the metallacycle in (**4**), *i.e.* contribution of the metallacyclobutadiene valence isomer. As a result of such a contribution the C=N bond order is lowered, enabling facile rotation of the bond to give the thermodynamically more stable isomer.[1]

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