Synthesis and Molecular Structure of 1-(π-Cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole

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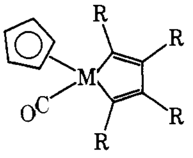
Abstract: The reaction of π-cyclopentadienylcarbonyl(triphenylphosphine)cobalt with bis(pentafluorophenyl)acetylene yields two products, π-cyclopentadienyltetrakis(pentafluorophenyl)cyclopentadienonecobalt and 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole, in yields of 21 and 49%, respectively. The latter, highly fluorinated compound has enhanced thermal stability compared to the hydrocarbon analogue. An indisputable structural assignment for cobalt-containing metallocycles of this type was obtained from an x-ray crystal-structure study of the title compound. Deep red crystals of the title compound from Skelly C are triclinic, with unit cell dimensions of a = 11.680 (3), b = 14.008 (4), and c = 20.455 (9) Å with α = 114.08 (3), β = 107.41 (3), and γ = 106.72 (2)°. There is an ill-defined molecule of solvent in the lattice which affects the agreement between the observed and calculated densities. The structure was solved by the heavy-atom method and refined by least-squares techniques to a residual R of 0.077 for the 5479 reflections with $I \geq 2\sigma(I)$ which were used in the analysis. The cobalt is σ-bonded to the two carbons of a butadiene-like fragment with Co-C of 1.993 (11) and 1.995 (11) Å. The C-C distances of 1.326 (15) and 1.335 (15) Å in the butadiene appear as isolated double bonds. The Co-P bond of 2.343 (3) Å is similar to that found in other cobalt-phosphine organometallic compounds. The remainder of the distances are normal.

Metal-containing heterocycles (or metallocycles) such as **1**, M = Co, Rh, and Ir,[2-5] have been implicated as intermediates in the reactions of acetylenes with π-cyclopentadienyldicarbonylmetal complexes, **2**, M = Co, Rh, and Ir.



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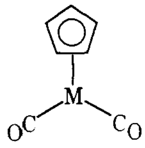

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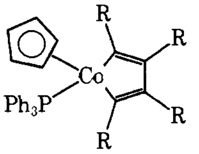
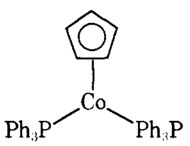


3a, R = C_6H_5
3b, R = C_6F_5



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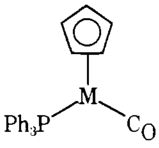

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Unfortunately, under the usual reaction conditions employed these metallocyclic intermediates are expected to be converted into more stable products. However, a related phosphine-containing cobaltacycle (**3a**) has been isolated from the reaction of diphenylacetylene with (π-C_5H_5)Co(PPh_3)I_2 and isopropylmagnesium bromide[6] or from the reaction of excess diphenylacetylene with (π-C_5H_5)Co$(PPh_3)_2$[7,8] (**4**). A metallocyclic structure was assigned to **3a** on the basis of chemical reactions. In view of the above results, stable metallocycles of the type **3** might be obtained from the reaction of (π-C_5H_5)M(PPh_3)(CO) (**5**, M = Co) with various acetylenes. Indeed, the reaction of bis(pentafluorophenyl)acetylene with (π-C_5H_5)Co(PPh_3)(CO) yields 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole (**3b**) as one of the products. The structure of **3b** was determined by x-ray diffraction techniques and is described below together with the synthesis and spectra of the compound. After completion of our study, a preliminary report of a similar cobaltacycle was published.[9]

Experimental Section

π-Cyclopentadienylcarbonyl(triphenylphosphine)cobalt was prepared by a literature method.[10] Bis(pentafluorophenyl)acetylene was prepared by a modification of a literature method.[11,12] Benzene and hexane were distilled under nitrogen from calcium hydride, and ethyl ether was distilled under nitrogen from sodium benzophenone before use. NMR spectra were recorded on a Perkin-Elmer R-12A instrument, ir spectra were recorded on a Beckman IR-10 instrument, and mass spectra were obtained with a Perkin-Elmer-Hitachi RMU 6L instrument operating at an ionizing potential of 70 eV. All melting points were taken under nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Mass. "Skelly C" is commercial heptane, br 88-98°.

Reaction of π-Cyclopentadienylcarbonyl(triphenylphosphine)cobalt and Bis(pentafluorophenyl)acetylene. A solution of bis(pentafluorophenyl)acetylene (2.60 g, 7.26 mmol) and π-cyclopentadienylcarbonyl(triphenylphosphine)cobalt (1.50 g, 3.62 mmol) in 25 ml of anhydrous benzene was refluxed for 23.5 h with magnetic stirring under nitrogen. The reaction was cooled and filtered under nitrogen to give 0.582 g of π-cyclopentadienyltetrakis(pentafluorophenyl)cyclopentadienonecobalt. An analytical sample was prepared by recrystallization from benzene-Skelly C, mp 315-317° (lit.[13,14] 311-312°). NMR ($CDCl_3$) τ 4.69 (broad s).

Anal. Calcd for $C_{34}H_5CoF_{20}O$: C, 47.03; H, 0.58; Co, 6.79; F, 43.76; O, 1.84; mol wt 868. Found: C, 47.10; H, 0.60; Co, 6.85; F, 43.80; O, 1.86; mol wt 868 (mass spectrometry).

To the red-brown filtrate was added 10 g of alumina (deactivated with 5% water) under nitrogen and the solvent was removed. The coated alumina was added to a dry alumina column (2 × 50 cm) packed under nitrogen.[15]

Elution with hexane followed by 3:1 hexane-benzene brought down a colorless band of unreacted bis(pentafluorophenyl)acetylene (0.333 g, 12.5% recovery). Further elution brought down a light yellow band (0.159 g). TLC of this band indicated it was predominantly triphenylphosphine.

Further elution with 3:1 hexane-benzene followed by 1:1 hexane-benzene gave a dark red band. The solvent was removed under vacuum and the residue recrystallized from methylene chloride-Skelly C to give 1.911 g (48.6%) of 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole (**3b**). An analytical sample of **3b** was obtained as deep red crystals by recrystallization from Skelly C and subsequent drying in vacuo overnight at 70°: mp 259-261° (N_2); NMR ($CDCl_3$) τ 5.13 (s, 5

Table I. Final Atomic Parameters for Heavy Atoms of 1-(π-Cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	482 (1)	4958 (1)	2130 (1)	65 (1)	64 (1)	24 (0)	55 (2)	32 (1)	46 (1)
C(1)	1469 (8)	4004 (8)	2096 (5)	78 (10)	71 (8)	27 (3)	70 (15)	32 (10)	52 (9)
C(2)	2439 (8)	4318 (8)	1903 (5)	89 (10)	78 (8)	26 (3)	95 (16)	51 10)	53 (9)
C(3)	2748 (8)	5385 (7)	1870 (5)	72 (9)	71 (8)	27 (3)	84 (15)	48 (10)	51 (9)
C(4)	1955 (8)	5881 (7)	2001 (5)	78 (10)	69 (8)	23 (3)	52 (15)	25 (9)	51 (9)
C(11)	1050 (9)	2894 (8)	2093 (5)	88 (10)	72 (8)	38 (4)	80 (16)	60 (11)	68 (10)
C(12)	1267 (9)	2877 (8)	2792 (6)	89 (11)	79 (9)	39 (4)	76 (16)	45 (11)	67 (10)
C(13)	889 (10)	1830 (9)	2778 (6)	135 (14)	116 (11)	51 (5)	134 (21)	89 (14)	117 (13)
C(14)	263 (12)	754 (9)	2043 (7)	168 (16)	87 (10)	68 (6)	135 (22)	117 (17)	107 (14)
C(15)	19 (11)	746 (9)	1333 (6)	151 (15)	80 (10)	47 (5)	116 (20)	97 (14)	60 (11)
C(16)	445 (10)	1799 (8)	1379 (6)	126 (13)	80 (9)	43 (4)	110 (18)	87 (13)	78 (11)
F(12)	1875 (6)	3866 (5)	3516 (3)	148 (8)	97 (5)	34 (2)	91 (11)	53 (7)	67 (6)
F(13)	1138 (7)	1855 (6)	3474 (4)	215 (10)	147 (7)	64 (3)	164 (14)	113 (10)	157 (9)
F(14)	−138 (8)	−275 (6)	2022 (5)	272 (12)	103 (7)	90 (4)	182 (15)	178 (13)	145 (9)
F(15)	−612 (7)	−301 (5)	622 (4)	239 (11)	78 (6)	65 (3)	112 (13)	132 (10)	62 (7)
F(16)	198 (6)	1719 (5)	670 (3)	182 (8)	87 (5)	37 (2)	106 (11)	88 (8)	54 (6)
C(21)	3171 (9)	3601 (8)	1668 (5)	106 (11)	71 (8)	33 (4)	87 (16)	56 (11)	58 (10)
C(22)	4034 (10)	3453 (9)	2197 (6)	123 (13)	95 (10)	42 (4)	135 (19)	68 (13)	67 (11)
C(23)	4718 (12)	2839 (11)	1981 (7)	145 (15)	140 (13)	59 (6)	190 (25)	75 (16)	103 (15)
C(24)	4545 (12)	2345 (11)	1201 (8)	154 (16)	126 (13)	78 (7)	198 (25)	128 (18)	99 (16)
C(25)	3682 (11)	2460 (9)	647 (6)	159 (15)	98 (11)	48 (5)	123 (22)	107 (15)	58 (12)
C(26)	3020 (10)	3081 (8)	885 (6)	118 (12)	84 (9)	42 (4)	103 (18)	68 (13)	69 (11)
F(22)	4250 (7)	3923 (6)	2967 (4)	188 (9)	145 (7)	47 (3)	216 (14)	75 (8)	100 (8)
F(23)	5532 (8)	2681 (8)	2501 (5)	237 (12)	215 (10)	81 (4)	346 (20)	104 (12)	152 (11)
F(24)	5233 (9)	1775 (8)	972 (5)	261 (13)	200 (10)	102 (5)	359 (20)	197 (14)	134 (12)
F(25)	3500 (8)	1971 (6)	−124 (4)	251 (12)	151 (8)	65 (4)	210 (16)	176 (11)	97 (9)
F(26)	2165 (6)	3179 (5)	329 (3)	177 (9)	111 (6)	37 (2)	143 (12)	79 (8)	71 (7)
C(31)	3869 (9)	5823 (7)	1701 (5)	92 (10)	63 (8)	33 (4)	77 (15)	50 (11)	56 (9)
C(32)	3655 (9)	5820 (8)	992 (6)	103 (12)	84 (9)	37 (4)	87 (17)	57 (12)	61 (11)
C(33)	4687 (11)	6121 (10)	789 (7)	161 (15)	119 (12)	55 (5)	151 (22)	135 (16)	110 (14)
C(34)	5991 (11)	6489 (10)	1326 (7)	113 (13)	125 (12)	73 (6)	123 (21)	132 (16)	118 (15)
C(35)	6264 (9)	6524 (9)	2038 (7)	80 (11)	109 (11)	63 (6)	108 (19)	80 (14)	92 (13)
C(36)	5234 (9)	6200 (9)	2213 (6)	104 (11)	92 (10)	39 (4)	111 (18)	59 (12)	72 (11)
F(32)	2390 (6)	5458 (5)	454 (3)	127 (7)	147 (7)	43 (3)	129 (12)	63 (7)	107 (7)
F(33)	4392 (7)	6050 (7)	81 (4)	225 (11)	199 (9)	67 (4)	212 (17)	174 (11)	169 (10)
F(34)	6973 (7)	6763 (7)	1127 (5)	178 (100)	213 (10)	111 (5)	200 (17)	224 (13)	206 (12)
F(35)	7531 (6)	6879 (7)	2557 (5)	100 (7)	181 (9)	93 (4)	158 (13)	99 (9)	154 (10)
F(36)	5552 (5)	6243 (6)	2923 (3)	106 (7)	157 (7)	47 (3)	125 (12)	48 (7)	112 (8)
C(41)	2261 (9)	7041 (8)	2072 (5)	91 (10)	75 (8)	33 (4)	95 (16)	64 (11)	61 (10)
C(42)	1472 (9)	7178 (8)	1482 (5)	107 (11)	90 (9)	31 (4)	104 (18)	50 (11)	65 (10)
C(43)	1764 (10)	8273 (9)	1579 (6)	137 (14)	109 (11)	49 (5)	150 (21)	81 (14)	109 (13)
C(44)	2816 (11)	9268 (9)	2269 (7)	143 (14)	79 (9)	61 (6)	110 (20)	106 (15)	95 (13)
C(45)	3644 (10)	9168 (8)	2845 (6)	105 (12)	79 (9)	45 (5)	54 (18)	70 (13)	57 (11)
C(46)	3377 (8)	8066 (8)	2729 (5)	78 (10)	68 (8)	32 (4)	54 (15)	39 (10)	52 (9)
F(42)	388 (5)	6210 (5)	778 (3)	129 (7)	110 (6)	35 (2)	99 (11)	34 (7)	78 (6)
F(43)	970 (7)	8332 (6)	986 (4)	213 (10)	152 (8)	74 (4)	214 (15)	100 (10)	166 (9)
F(44)	3063 (8)	10324 (6)	2369 (5)	236 (11)	96 (6)	93 (4)	155 (14)	133 (12)	131 (9)
F(45)	4746 (6)	10156 (5)	3532 (4)	162 (9)	81 (6)	61 (3)	35 (11)	75 (9)	55 (7)
F(46)	4247 (5)	8032 (5)	3315 (3)	100 (6)	94 (5)	38 (2)	68 (10)	34 (6)	63 (6)
C(51)	−1476 (9)	4842 (10)	1969 (6)	63 (10)	125 (11)	40 (4)	70 (18)	22 (11)	77 (12)
C(52)	−1486 (9)	3709 (9)	1766 (6)	64 (10)	112 (11)	50 (5)	26 (18)	25 (12)	90 (13)
C(53)	−1196 (10)	3326 (9)	1116 (6)	99 (12)	84 (10)	34 (4)	61 (18)	10 (12)	41 (11)
C(54)	−929 (9)	4195 (8)	911 (5)	88 (11)	89 (9)	29 (4)	81 (17)	21 (11)	40 (10)
C(55)	−1115 (9)	5132 (9)	1426 (6)	77 (11)	111 (10)	35 (4)	80 (18)	19 (11)	73 (11)
P	1381 (2)	6265 (2)	3462 (1)	72 (3)	71 (2)	26 (1)	61 (4)	39 (3)	52 (2)
C(60)	174 (9)	5972 (8)	3855 (5)	77 (10)	97 (10)	30 (4)	67 (16)	44 (10)	61 (10)
C(61)	−309 (10)	4875 (10)	3800 (6)	118 (13)	117 (11)	53 (5)	95 (20)	87 (14)	109 (13)
C(62)	−1268 (12)	4596 (11)	4068 (8)	143 (15)	158 (15)	66 (6)	103 (25)	119 (17)	140 (17)
C(63)	−1740 (12)	5396 (12)	4382 (8)	160 (17)	160 (15)	65 (6)	126 (26)	134 (18)	121 (17)
C(64)	−1260 (14)	6475 (12)	4438 (8)	206 (20)	158 (16)	80 (8)	182 (30)	202 (22)	129 (19)
C(65)	−281 (11)	6770 (10)	4179 (7)	156 (15)	130 (12)	59 (6)	161 (23)	140 (16)	105 (14)
C(70)	2931 (9)	6458 (8)	4204 (5)	93 (11)	67 (8)	30 (4)	53 (16)	30 (11)	53 (10)
C(71)	3110 (10)	6734 (9)	4984 (6)	130 (13)	96 (10)	33 (4)	76 (19)	47 (12)	72 (11)
C(72)	4288 (11)	6884 (10)	5544 (6)	121 (14)	122 (12)	42 (5)	56 (21)	24 (13)	92 (13)
C(73)	5256 (11)	6731 (10)	5313 (7)	113 (14)	128 (13)	54 (5)	81 (22)	22 (14)	102 (14)
C(74)	5079 (10)	6465 (10)	4545 (6)	102 (13)	116 (12)	46 (5)	92 (20)	27 (13)	74 (13)
C(75)	3935 (9)	6342 (8)	3993 (6)	76 (10)	85 (9)	38 (4)	72 (16)	32 (11)	58 (10)
C(80)	1783 (9)	7786 (8)	3738 (5)	101 (11)	77 (9)	31 (4)	84 (16)	66 (11)	58 (10)
C(81)	857 (9)	7958 (8)	3226 (6)	109 (12)	93 (10)	41 (4)	115 (18)	77 (12)	76 (11)
C(82)	1115 (11)	9122 (10)	3440 (7)	144 (14)	112 (11)	54 (5)	154 (21)	107 (15)	100 (13)
C(83)	2298 (11)	10114 (10)	4154 (7)	143 (15)	99 (11)	58 (6)	109 (21)	103 (16)	81 (13)
C(84)	3216 (11)	9918 (9)	4656 (7)	137 (14)	84 (10)	53 (5)	80 (20)	81 (15)	69 (12)
C(85)	2968 (10)	8774 (9)	4448 (6)	113 (12)	83 (10)	38 (4)	65 (18)	58 (12)	58 (11)

[a] The values have been multiplied by 10^4. The estimated standard deviations are given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

H, π-C_5H_5), 2.53–3.19 (m, 15 H, Ph); ir (KBr) 1472 (s), 1435 (w), 1107 (w), 1085 (m), 982 (s), 937 (m), 823 (w), 745 (w), and 693 (w) cm^{-1}. Mass spectrum *m/e* (%) 1102 (3.7, M^+), 840 (23, $C_5H_5Co(C_6F_5C_2C_6F_5)^+$), 821 (1.9, $C_5H_5Co(C_6F_5C_2C_6F_5) - F^+$), 420 (5.4, $C_5H_5Co(C_6F_5C_2C_6F_5)^{2+}$), 358 (38, $C_6F_5C_2C_6F_5^+$), 262 (100, $(C_6H_5)_3P^+$), 124 (25, $C_5H_5Co^+$), 59 (32, Co^+).

Anal. Calcd for $C_{51}H_{20}CoF_{20}P$: C, 55.56; H, 1.83; Co, 5.35; P, 2.81. Found: C, 55.48; H, 2.51; Co, 5.69; P, 2.56.

Elution with benzene gave several bands containing small amounts (less than 5 mg) of one or more compounds which were not characterized.

Further elution with 1:1 benzene–ethyl ether gave a dark red band (0.159 g). The solvent was removed, the residue dissolved in methylene chloride and 1 g of alumina added, and the solvent again removed. This material was added to a dry alumina column (2 × 15 cm). Elution with 9:1 benzene–ether gave a red band (0.054 g) which by TLC was shown to consist of several compounds and was not further characterized. Elution with 3:1 benzene–ether gave another red band which upon evaporation of the solvent afforded 0.083 g of π-cyclopentadienyltetrakis(pentafluorophenyl)cyclopentadienonecobalt.

Elution of the initial alumina column with ethyl ether gave a red band which upon evaporation of the solvent afforded 9 mg of additional π-cyclopentadienyltetrakis(pentafluorophenyl)cyclopentadienonecobalt, for a total yield of this complex of 21.4%.

Crystallographic Studies. Deep red crystals of **3b** were grown from Skelly C. Preliminary precession photographs indicated that the crystals were triclinic. A crystal 0.27 × 0.31 × 0.50 mm was mounted on a Syntex P1 diffractometer. Unit cell dimensions determined from a least-squares fit of 15 reflections are a = 11.680 (3), b = 14.008 (4), and c = 20.455 (9) Å with α = 114.08 (3), β = 107.41 (3), and γ = 106.72 (2)°. The unit cell volume is 2572.9 (1.7) Å^3. For two molecules of $CoPF_{20}C_{51}H_{20}$, mol wt is 1102.79, the calculated density of 1.423 g cm^{-3} does not agree with the observed value of 1.59 g cm^{-3}. However, as discussed below there is an ill-defined molecule of solvent in the crystal and the value should be nearer to 1.57 g cm^{-3}, calculated assuming two molecules of C_8H_{18} per unit cell. Intensity statistics subsequently indicated that the space group was $P\bar{1}$, a choice which was supported by our successful analysis. Intensity measurements were made using a θ–2θ scan with a variable scan rate (2°/min for intensities >150 counts/sec and 24°/min for intensities >1500 counts/sec with a linear interpolation for intermediate values) for all reflections with $2\theta < 45°$. The radiation was graphite monochromatized Mo Kα radiation (α_1 = 0.70926 and α_2 = 0.71354 Å). The scan range was from 1° below the α_1 peak to 1° above the α_2 peak. Background was measured at each end of the scan range for a time equal to one-half the scan time. A total of 6772 reflections was measured of which the 5479 reflections with $I \geq 2\sigma(I)$ were considered observed and used in the analysis. The remaining 1293 reflections were flagged with a minus sign, assigned a value of $0.5\sigma(I)$, and were not used in the analysis. These data were then reduced to a set of structure amplitudes on an arbitrary scale by the application of Lorentz-polarization factors, assuming that the monochromator was a 50% mosaic and 50% perfect crystal.

Solution and Refinement of the Structure. A sharpened three-dimensional Patterson function was calculated and used to determine the position of the Co atom. Since the intensity statistics favored the space group $P\bar{1}$, a Fourier synthesis was computed assuming the centric space group and using phases determined by the Co atom. The remaining non-hydrogen atoms were located in two successive Fourier syntheses. After three full-matrix least-squares cycles R, the usual residual, was reduced from 0.27 to 0.14. The thermal parameters were converted to their anisotropic equivalent, and six least-squares cycles using a block approximation to the matrix reduced R to 0.077. A difference Fourier synthesis calculated at this stage suggested the presence of an ill-defined solvent molecule between the cobaltacycles. The peaks were not well resolved but the heights and distribution suggested a C_7 or C_8 chain. Unfortunately, attempts to fit a linear molecule to these peaks were unsuccessful and were not pursued. However, the inclusion of a C_8 fragment would make the calculated density in better agreement with the observed value. Since the shifts in the non-hydrogen atom parameters in the last least-squares cycle were all less than one-tenth of an estimated standard deviation, the refinement was terminated at this point. The final positional and thermal parameters for the non-hydrogen atoms are given in Table I.

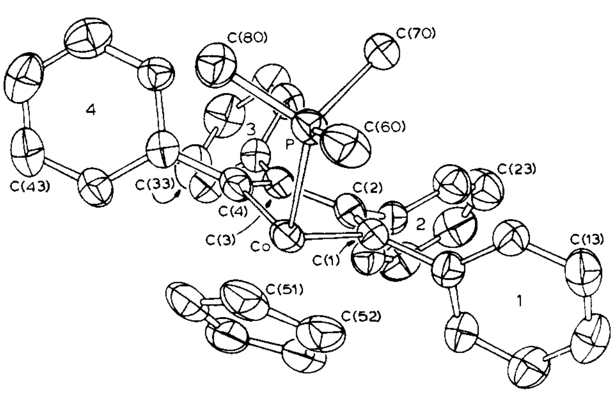

Figure 1. The atomic numbering and thermal ellipsoids in 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole. The pentafluorophenyl rings are numbered 1–4 and the fluorines have been omitted for clarity. Similarly, the three phenyl rings of the phosphine have been omitted with only the first atoms C(60), C(70), and C(80) being shown. The cobaltacycle is best viewed as a cyclopentadiene with the double bonds between C(1)–C(2) and C(3)–C(4).

The quantity minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was $\sqrt{w} = |F_o| / 17.5$, if $|F_o| < 17.5$, $\sqrt{w} = 1$ if $17.5 \leq |F_o| \leq 35.0$, and the $\sqrt{w} = 35.0/F_o$ if $F_o > 35.0$. Scattering factors were taken from the usual sources,[16] and all calculations were carried out with programs written or modified by G.J.P. A list of the observed and calculated structure factors is available.[17]

Results and Discussion

Although reactions between acetylenes and organometallic complexes of the types **2** and **4** have been extensively investigated, the corresponding reactions between acetylenes and **5** have been ignored. In the reactions involving **5** two different products are possible depending on whether the phosphine or carbonyl group is displaced by the acetylene. Remarkably, in the reaction of bis(pentafluorophenyl)acetylene with **5**, M = Co, both products, π-cyclopentadienyltetrakis(pentafluorophenyl)cyclopentadienonecobalt and 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole (**3b**), are obtained in yields of 21 and 49%, respectively. Although both products were characterized by the usual methods, because of the unique nature of **3b**, an x-ray crystal structure (vide infra) was carried out to elucidate the structure unequivocally.

The atomic number and the thermal ellipsoids of the cobaltacycle are shown in Figure 1. Selected distances and angles are given in Tables II and III. The molecule is a cobaltacycle with the cobalt also bonded to the triphenylphosphine ligand (Co-P is 2.234 (3) Å) and the cyclopentadienyl ring (C(51)–C(55)). The C(1) to C(4) fragment is planar with deviations from the best plane of 0.008, −0.015, 0.015, and 0.008 Å, respectively. However, the cobalt atom is displaced by −0.203 Å from the plane in the direction of the Cp ring. The Cp ring is also planar but tipped by 35.3° relative to the C(1) to C(4) plane. In addition, the Co–C (to Cp ring) distances show that the cobalt atom is slightly displaced from the center of the Cp ring. The P-Co-C(1) and P-Co-C(4) angles of 103.0 (3) and 95.2 (3)°, respectively, indicate that the triphenylphosphine group is bent away from the cobaltacycle ring. The tip of the triphenylphosphine, the displacement of the cobalt atom from the C(1)–C(4) ring, and the orientation of the Cp ring may all be related to steric constraints in the molecule. The triphenylphosphine ligand together with the four C_6F_5 rings provide an effective shield for the two double bonds in the cobaltacycle which may explain the stability of the intermediates.

Table II. Selected Bond Distances of 1-(π-Cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole

Atoms	Dist, Å	Atoms	Dist, Å
Co–C(1)	1.995 (11)	C(1)–C(11)	1.487 (16)
Co–C(4)	1.993 (11)	C(2)–C(21)	1.523 (16)
Co–P	2.234 (3)	C(3)–C(31)	1.481 (15)
Co–C(51)	2.157 (12)	C(4)–C(41)	1.493 (16)
Co–C(52)	2.121 (13)	P–C(60)	1.848 (11)
Co–C(53)	2.119 (11)	P–C(70)	1.843 (11)
Co–C(54)	2.104 (9)	P–C(80)	1.834 (12)
Co–C(55)	2.133 (12)	C(51)–C(52)	1.463 (20)
C(1)–C(2)	1.326 (15)	C(52)–C(53)	1.400 (16)
C(2)–C(3)	1.467 (16)	C(53)–C(54)	1.426 (18)
C(3)–C(4)	1.335 (15)	C(54)–C(55)	1.433 (16)
		C(55)–C(51)	1.457 (17)

Average C–F and C–C Distances for Pentafluorophenyl Rings with Estimated Standard Deviations[a] in Parentheses

	C–F dist, Å	C–C dist, Å
	1.344 (2)	1.378 (3)
Ring 1	1.342 (7)	1.385 (3)
Ring 2	1.345 (4)	1.372 (5)
Ring 3	1.340 (3)	1.384 (8)
Ring 4	1.348 (4)	1.372 (8)

[a] Standard deviations were estimated from

$$\sigma = \sum_{i=1}^{i=N} (X_i - \overline{X})^2/N(N-1)\}^{1/2}.$$

Table III. Selected Bond Angles of 1-(π-Cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)cobaltole

Atoms	Angle, deg	Atoms	Angle, deg
Co–C(1)–C(2)	112.1 (8)	C(41)–C(4)–C(3)	119.8 (9)
C(1)–C(2)–C(3)	116.8 (9)	C(41)–C(4)–Co	127.0 (7)
C(2)–C(3)–C(4)	114.8 (9)	C(51)–C(52)–C(53)	108.1 (11)
Co–C(4)–C(3)	113.1 (7)	C(52)–C(53)–C(54)	109.8 (10)
C(1)–Co–C(4)	82.4 (4)	C(53)–C(54)–C(55)	107.7 (10)
C(11)–C(1)–Co	127.0 (7)	C(54)–C(55)–C(51)	108.0 (10)
C(11)–C(1)–C(2)	119.6 (9)	C(55)–C(51)–C(52)	106.3 (10)
C(21)–C(2)–C(1)	123.9 (9)	C(60)–P–C(70)	102.7 (5)
C(21)–C(2)–C(3)	119.2 (9)	C(60)–P–C(80)	100.9 (5)
C(31)–C(3)–C(2)	119.7 (9)	C(70)–P–C(80)	103.0 (5)
C(31)–C(3)–C(4)	125.5 (9)	P–Co–C(1)	103.0 (3)
P–Co–C(4)	95.2 (3)		

The cobaltacycle can be viewed as a delocalized diene with the cobalt σ bonded to the two carbon atoms C(1) and C(4) of the ring. The Co-C bonds are 1.995 (11) and 1.993 (11) Å which are similar to the various values given by Churchill.[18] More recently the values of 1.979 (1)[19] and 1.990 (5) Å[20] were reported for Co-C bonds in some cobaloxime complexes. Therefore, the available structure evidence supports the hypothesis that the cobalt is σ bonded to the ring. The C-C distances in the ring fall into two groups: C(1)-C(2) and C(3)-C(4) are 1.326 (15) and 1.335 (15) Å, respectively, which is identical with the accepted value of 1.337 (6) Å for a simple CC double bond,[21] and C(2)-C(3) of 1.487 (16) Å, indicative of a single bond between two double bonds.[21] Although no structural data on an analogous cobalt compound are available, an interesting comparison can be made with some rhodium complexes. The work by Mague[22,23] on two rhodiacyclopentadiene complexes suggested a localized double bond system similar to the cobaltacycle. However, in a polynuclear Rh complex the localized character of the ring was not as obvious which may reflect the interaction of other Rh atoms with the C_4 fragment.[24] However, the evidence to date suggests that in simple metallocycles of Co and Rh the C_4 moiety is best considered as a butadiene fragment.

The Co-P distance of 2.234 (3) Å is shorter than the values of 2.327 (4)[25] and 2.339 (1) Å[19] found in cobaloxime complexes. The difference is somewhat surprising in view of the difference in the formal oxidation state in the compounds. However, a comparison with cobalt carbonyl complexes such as $Co_4(CO)_{10}(Ph_2PC{\equiv}CCF_3)_2$ where Co-P is 2.236 and 2.229 Å[26] or $Co(CO)_2(NO)(PPh_3)$ where Co-P bond is 2.224 (3)[26] and 2.230 (3) Å[27] suggests that the Co-P bond distance is the same in all the organometallic type complexes. The longer Co-P bond in the cobaloximes may be a steric or electronic effect but this choice cannot be made at present.

The distances in the pentafluorophenyl rings have been summarized in Table II. The individual values for distances and angles in the pentafluorophenyl rings on the cobaltacycle and the phenyl rings of the phosphine are given in Tables IV and V and are available.[17] The dimensions are not unusual and are in agreement with the expected values.

The fluorinated cobaltacycle **3b** has an enhanced thermal stability compared to the hydrocarbon analogue **3a.** For example, while **3b** is stable in refluxing benzene, under identical conditions **3a** decomposes to π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt.[28,29] Furthermore, a weak but discernible parent peak is observed in the mass spectrum of **3b** while all attempts to obtain a mass spectrum of **3a** have failed to give the parent ion peak, with the first major peak being due to the decomposition product π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt. Enhanced stabilities of highly fluorinated metallocycles relative to the hydrocarbon analogues have been observed in related studies.[30]

Although the fluorine atoms were not included in Figure 1, the sterically hindered nature of the cobaltacycle is easily seen. The isolation of these intermediate cobaltacycles may be related to the lack of a convenient path for an attacking acetylene together with enhanced thermal stability of the fluorinated derivatives. In any case the results of the present study clearly demonstrate that cobaltacycles are reasonable intermediates in organometallic reactions.

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Supplementary Material Available: a table of distances and angles in the pentafluorophenyl groups and the phenyl rings of the phosphine ligand together with a comparison of the observed and calculated structure factor amplitudes (27 pages). For ordering information consult any current masthead page.

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Kinetic Study of the Copper(II)-Catalyzed Enolization, Ketonization, and Decarboxylation of Oxaloacetate[1]

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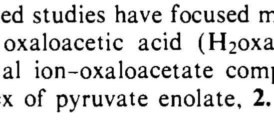
Abstract: Cu(II) and oxaloacetate, oxac^{2-}, react rapidly in solution to form Cu(oxac)$_{\mathrm{keto}}$ which enolizes and decarboxylates via competing reaction paths. Because the two processes proceed at comparable rates, and enolization is reversible, the evolution of CO_2 from these reaction mixtures is observed to be biphasic, the slower rate limited by the reketonization of Cu(oxac)$_{\mathrm{enol}}$. In this respect catalysis by Cu(II) differs from that reported for other metal ions where only the slower step has been observed. The presence of a fast decarboxylation step has made it possible to obtain the true rate constant for the decarboxylation of Cu(oxac)$_{\mathrm{keto}}$ and also to observe the reaction kinetics of the short-lived intermediate, Cu(pyr)$_{\mathrm{enolate}}$ (pyr = pyruvate). Evaluation of the equilibrium constant for the reaction Cu(oxac)$_{\mathrm{keto}}$ $\rightleftarrows$ Cu(oxac)$_{\mathrm{enol}}$ is also made possible by the biphasic nature of CO_2 evolution. The consumption of H$^+$ which accompanies the conversion of the intermediate to Cu(pyr) was also found to be biphasic, the rate at shorter times depending on the kinetics of pyruvate formation and at longer times, like slow CO_2 evolution, being determined by the reketonization of Cu(oxac)$_{\mathrm{enol}}$. A proton-catalyzed and an uncatalyzed reaction path were found for the enolization of Cu(oxac)$_{\mathrm{keto}}$. The rate of protonation of Cu(pyr)$_{\mathrm{enolate}}$ was found to be independent of pH, indicating that Cu(II)-oxygen bond breaking associated with ligand rearrangement is rate limiting. Inhibition of decarboxylation at high Cu(II) concentrations arises from the formation of polynuclear Cu(II) complexes of oxac$_{\mathrm{enolate}}^{3-}$. A detailed quantitative description of the reaction system has been obtained and is reported.

Similarities between enzymatic and metal ion catalyzed decarboxylation processes have for a number of years stimulated investigations of the metal ion catalyzed reactions with the hope of shedding light on the enzymatic systems.[2-9] Detailed studies have focused mainly on the decarboxylation of oxaloacetic acid (H_2oxac) and its derivatives.[10-18] Metal ion-oxaloacetate complexes lose CO_2 to form a complex of pyruvate enolate, **2**. This latter species



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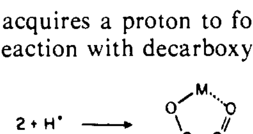
rearranges and acquires a proton to form pyruvate, **3**.[10-18] A competitive reaction with decarboxylation comprises the



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formation of oxac$_{\mathrm{enol}}^{2-}$,[4-11] which does not decarboxylate.[11-17]

In studying the decarboxylation of α,α-dimethyloxaloacetate, Steinberger and Westheimer[11] noted that a biphasic absorbance change occurs in the ultraviolet region. Since α,α-dimethyloxaloacetate cannot enolize, an initial increase in absorbance was attributed to the formation of the immediate decarboxylation product, the dimethyl derivative of pyruvate enolate. The succeeding absorbance decrease was then assigned to protonation and ketonization of the intermediate. A similar sequence of absorbance changes is noted for the metal ion catalyzed decarboxylation of oxac^{2-}; however, the enolization of oxac^{2-} itself complicates the interpretation. Gelles and Hay[12] and Gelles and Salama[13] claim that oxac^{2-} enolization is fast compared to the CO_2 loss so that the observed absorbance changes arise from the Steinberger-Westheimer reaction sequence. Others have ascribed these changes to the formation of oxac^{2-} enol and enolate complexes[4,14,16] which ultimately disappear as decarboxylation proceeds.

Until a recent quantitative study of the influence of Zn(II) on the oxac^{2-} reactions appeared[18] very little had been reported regarding the influence of metal ions on the enolization rates. It was shown[18] that an increase in uv absorbance which is complete in about 30 s after mixing Zn(II) and oxac^{2-} solutions arises from the conversion of Zn(oxac)$_{\mathrm{keto}}$ (**1**) to Zn(oxac)$_{\mathrm{enol}}$ (**4**). A subsequent slower absorbance decrease proceeds at the same rate as CO_2 loss. The protonation of intermediate Zn(pyr)$_{\mathrm{enolate}}$ (**2**) is sufficiently fast that it is rate limited by decarboxylation and is not observed. Thus, the reaction sequence found by Steinberger and Westheimer does not account for the absorbance changes in the Zn(II)-oxac^{2-} systems. Because the rate of decarboxylation is relatively slow, enolization essentially comprises a preequilibrium step, and therefore, as Gelles