Journal of Organometallic Chemistry, 344 (1988) 393–400
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis and crystal structure of the $[CoRu_3(\mu\text{-}CO)_2(CO)_9(\mu_4,\eta^2\text{-}C_2Ph_2)][PPN]$ cluster

Ouassini Benali-Baitich, Jean-Claude Daran and Yves Jeannin

*Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie,
75230 Paris Cedex 05 (France)* *

(Received October 12th, 1987)

Abstract

Reaction of C_2Ph_2 with $[CoRu_3(CO)_{13}](PPN)$ affords the violet butterfly complex $[CoRu_3(\mu\text{-}CO)_2(CO)_9(\mu_4,\eta^2\text{-}C_2Ph_2)](PPN)$, which crystallizes in triclinic space group $P\bar{1}$, a 9.9840(8) Å, b 15.462(2) Å, c 19.572(3) Å, α 75.08(1)°, β 75.15(1)°, γ 87.85(3)°, V 2821(1) Å^3, $Z = 2$. This study completes the series of structures of ruthenium-cobalt *closo*-M_4C_2 clusters.

Introduction

The ready cleavage of one of the P–C bonds of diphenylphosphinoacetylene (dppa), generates complexes containing the alkynyl group $C{\equiv}CPPh_2$, which often is in extended interaction with several metal atoms [1]. Thus, dppa reacts thermally with $Ru_3(CO)_{12}$, or $Os_3(CO)_{12}$ to give open M_5 clusters in which a diphenylphosphinoethynyl ligand interacts with the five metal atoms [2,3]. These interesting pentanuclear clusters show unusual reactivity towards small molecules such as CO or H_2 [4,5,6]. We decided to synthesize similar open pentanuclear clusters containing mixed metals. One of the approaches we adopted involved starting from a mixed metal cluster, and in the first attempt we used the ruthenium-cobalt tetrahedral cluster anion $[CoRu_3(CO)_{13}]^-$ (with a $[N(P(C_6H_5)_3)_2]^+$ counterion [PPN]), thermal reactions of which in various solvents had been unproductive. To investigate reactivity of this stable cluster, we treated it with the simple alkyne diphenylacetylene, and we report here the isolation and the X-ray structural determination of the anion $[CoRu_3(CO)_{11}C_2Ph_2]^-$ so obtained. This study means that structural

---

* Present address: Laboratoire de Chimie de Coordination, Institut de Chimie, U.S.T.H.B. Boite Postale 31 El Alia, Bab Ezzouar-Alger (Algérie).

0022-328X/88/$03.50

information is now available for the whole series of butterfly clusters $[Co_4(CO)_{10}C_2Et_2]$ [7], $[Co_3Ru(CO)_{10}C_2Ph_2]^-$ [8], $[Co_2Ru_2(CO)_{11}C_2Ph_2]$ [9] and $[Ru_4(CO)_{12}C_2Ph_2]$ [10].

Discussion

The molecular structure of the anion of $[CoRu_3(\mu\text{-}CO)_2(CO)_9C_2(C_6H_5)_2](PPN)$ is shown in Fig. 1 together with the numbering scheme. Of the two possible isomers, one with a cobalt atom on the hinge and the other one with Co on the wing tip, the reaction evidently leads only to the latter. The alkyne has been inserted between cobalt and ruthenium in the $CoRu_3$ tetrahedron to open the cluster and form a *closo*-Ru_3CoC_2 cluster. This distorted octahedron is consistent with Wade's skeletal electron counting rules [11], which predict a *closo*-M_4C_2 structure with six vertices. For comparison structural data for other ruthenium-cobalt clusters having analogous M_4C_2 frameworks are presented in Table 1.

The metal atoms can be described as being in a "butterfly" configuration (Fig. 1) with a dihedral angle of 112.4° along the "hinge". This angle is slightly but significantly smaller than corresponding angles in the other complexes listed in Table 2, but the effectively identical value of 112.7° was found for $[FeRu_3(CO)_{12}\{C_2(C_6H_5)_2\}]$ [12]. Two bridging CO ligands span the Ru(1)–Ru(3) and Co(4)–Ru(3) edges, resulting in a shortened Ru(1)–Ru(3) distance of 2.6679(9) Å. However, as observed in other ruthenium-cobalt clusters, the bridging CO groups do not affect the Ru–Co bond length: the CO bridged Ru(3)–Co(4) distance is 2.5923(8) Å, whereas the non-bridged Ru(2)–Co(4) distance is 2.5833(9) Å. There is a semibridging CO between Co(4) and Ru(2), (Co(4)–C(43)–O(43) 169.3(7)°; Ru(2)–C(43) = 2.740(7) Å), and this is consistent with the IR data.

Table 1

Important bond lengths in the M_4C_2 framework for relevant ruthenium-cobalt clusters ($L' = C_2Et_2$, $L = C_2Ph_2$)

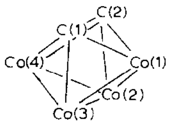
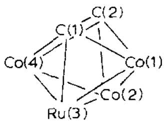
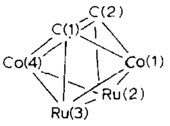
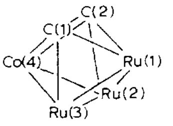
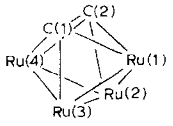
	$[Co_4(CO)_{10}L']$	$[Co_3Ru(CO)_{10}L]^-$	$[Co_2Ru_2(CO)_{11}L]$	$[CoRu_3(CO)_{11}L]^-$	$[Ru_4(CO)_{12}L]$
					
M(1)–M(2)	2.450(5)	2.481(2)	2.607(1)	2.8165(6)	2.74(1)
M(1)–M(3)	2.433(5)	2.525(2)	2.587(1)	2.6679(7)	2.71(1)
M(2)–M(3)	2.552(5)	2.725(2)	2.757(1)	2.8118(6)	2.85(1)
M(2)–M(4)	2.438(5)	2.518(2)	2.614(1)	2.5833(9)	2.71(1)
M(3)–M(4)	2.416(5)	2.493(2)	2.572(1)	2.5923(8)	2.74(1)
M(1)–M(4)	3.547(5)	3.549(2)	3.524(1)	3.7625(8)	3.93(1)
M(2)–C(2)	2.01(1)	2.14(1)	2.166(3)	2.141(5)	2.16(1)
M(3)–C(1)	2.01(1)	2.13(1)	2.278(3)	2.247(5)	2.16(1)
M(1)–C(1)	2.18(1)	2.07(1)	2.048(3)	2.236(5)	2.24(1)
M(1)–C(2)	2.03(1)	2.14(1)	2.101(3)	2.287(5)	2.24(1)
M(4)–C(1)	2.03(1)	2.12(1)	2.024(3)	2.048(5)	2.25(1)
M(4)–C(2)	2.15(1)	2.06(1)	2.102(3)	2.161(5)	2.26(1)

Table 2

Angles between M–C(alkyne) and M–C(O) bonds involving the CO groups *trans* to the alkyne. Comparison between bridging CO and terminal CO, and correlation with the M–C(alkyne) bond lengths

		M(3)–C(O)	M(3)–C(1)	M(2)–C(2)	M(2)–C(O)
$[Ru_3Co(CO)_{11}(C_2Ph_2]$	CO-bridging	166.1	2.247	2.141	151.2
$[Ru_4(CO)_{10}(PPh)(PhC_2PPh_2)]$	CO-bridging	175.7	2.24	2.06	137.1
$[FeCo_3(CO)_9\{PhC_2(H)Ph\}(C_2Ph_2)]$	CO-bridging	171.5	2.092	1.974	157.1
$[FeRu_3(CO)_{12}(C_2Ph_2)]$		152.4	2.16	2.16	152.4
$[Ru_4(CO)12(C_2Ph_2)]$		152.4	2.16	2.16	155.4

The ^{13}C NMR spectrum shows in addition to a multiplet around δ 129 ppm arising from phenyl groups, two sharp resonances with equivalent intensity at δ 157.5 and 179 ppm, and a very broad resonance at 206 ppm (Fig. 2). The broad signal can be attributed to CO groups, and the two singlets have chemical shifts consistent with those observed in μ_2-η^2 or μ_3-η^2 type alkyne-cluster complexes [13,14]. The appearance of two signals suggests that the alkyne carbon atoms C(1) and C(2) are not equivalent in solution, and this is, of course, the case in the solid state, in which the Ru(3)–C(1) and Ru(2)–C(2) bonds have different lengths, viz. 2.247(5) and 2.141(5) Å, respectively. Such dissimilar bonds were previously observed in $[Ru_2Co_2(CO)_{11}(C_2Ph_2)]$ (2.278(3) and 2.166(3) Å) and in $[Ru_4(CO)_{10}(PPh)(C_2PhPPh_2)]$ (2.24(2) and 2.06(1) Å) [15]. In all these complexes the longest Ru–C(σ-alkyne) bond refers to the metal atom involved in CO-bridged metal–metal bonds. It is noteworthy that, as can be seen from Table 2, the presence

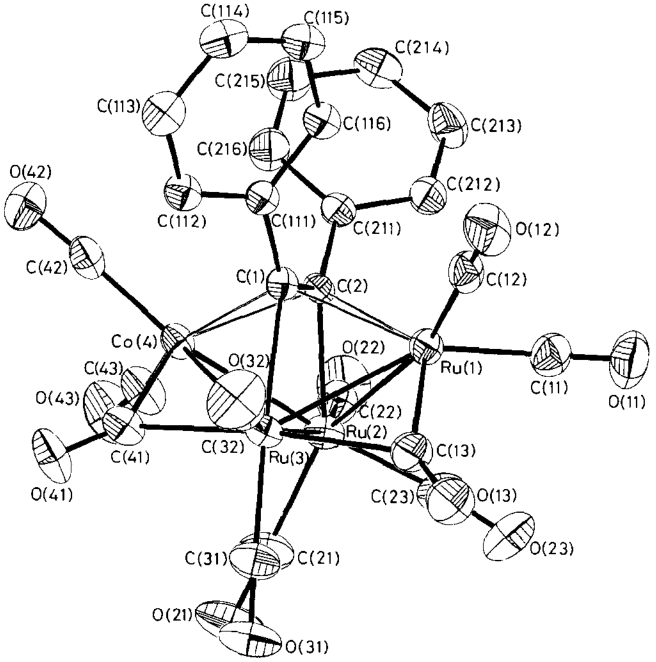


Fig. 1. Thermal ellipsoid diagram (30% probability) for the anion, and labelling scheme.

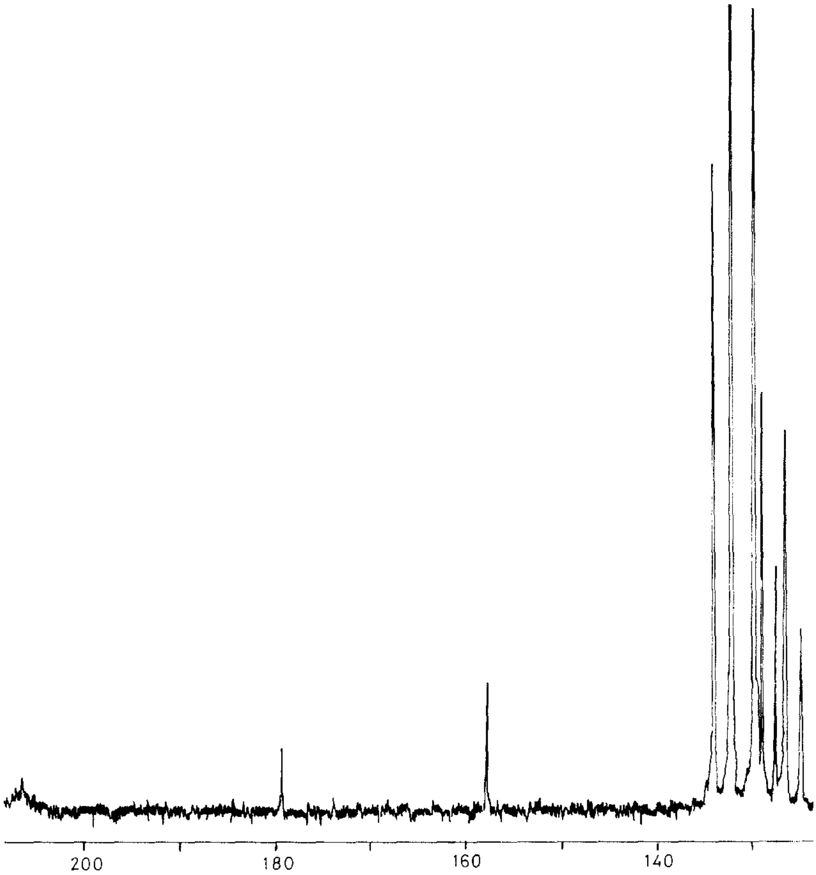


Fig. 2. ^{13}C NMR spectrum of the cluster in $CDCl_3$.

of such CO bridges changes the geometry around the central metal atom M(3), bringing one CO group closer to a *trans* position with respect to the C(alkyne) carbon atom. Thus, back donation from the CO group to metal *d* orbitals is enhanced, and the lengthening of the Ru–C(alkyne) may be the result of an electronic *trans* influence.

Experimental

All reactions were carried out under dry nitrogen. Acetone was dried over calcium hydride and stored over molecular sieves. $[Co(CO)_4](PPN)$ was prepared by a published procedure [16] from $Co_2(CO)_8$ that had been sublimed before use. Cluster I, $[Ru_3Co(CO)_{13}][PPN]$, was prepared by treatment of $[Ru_3(CO)_{12}]$ with $[Co(CO)_4][PPN]$ [17], and identified from its IR spectrum.

Infrared spectra (KBr pellets) were recorded with a Perkin–Elmer 597 spectrometer. ^{13}C NMR spectra were recorded with a WM 500 Bruker spectrometer.

Preparation of $[CoRu_3(CO)_{11}C_2(C_6H_5)_2][PPN]$

A mixture of $[CoRu_3(CO)_{13}][PPN]$ (I) (200 mg, 0.158 mmol) and $C_2(C_6H_5)_2$ (28 mg, 0.158 mmol) in refluxing acetone (50 ml) was stirred for 6 h. The initially red

Table 3

Fractional atomic coordinates and equivalent values of the anisotropic temperature factor coefficients, with e.s.d.s in parentheses

$U_{eq} = [U_{11} \times U_{22} \times U_{33}]^{1/3}$

Atom	x	y	z	U_{eq}
RU(1)	0.05704(5)	0.16688(3)	0.20025(3)	0.0427
RU(2)	−0.04651(5)	0.34060(3)	0.18851(3)	0.0429
RU(3)	−0.20136(5)	0.19351(3)	0.18646(2)	0.0383
CO(4)	−0.26107(8)	0.27189(5)	0.29230(4)	0.0372
C(11)	0.2469(8)	0.1853(5)	0.1598(4)	0.0632
O(11)	0.3650(6)	0.1935(5)	0.1341(3)	0.0899
C(12)	0.0890(6)	0.0457(5)	0.2290(3)	0.0518
O(12)	0.1013(6)	−0.0304(3)	0.2450(3)	0.0742
C(13)	−0.0121(7)	0.1494(5)	0.1205(4)	0.0576
O(13)	0.0155(6)	0.1240(4)	0.0675(3)	0.0775
C(21)	−0.1424(9)	0.4167(5)	0.1234(4)	0.0678
O(21)	−0.2019(8)	0.4600(4)	0.0855(4)	0.0931
C(22)	0.0254(7)	0.4325(4)	0.2208(4)	0.0553
O(22)	−0.4588(6)	0.2241(4)	0.4347(3)	0.0811
C(23)	0.1066(8)	0.3438(4)	0.1073(4)	0.0589
O(23)	0.1953(6)	0.3566(4)	0.0554(3)	0.0802
C(31)	−0.2402(8)	0.2451(5)	0.0954(4)	0.0609
O(31)	−0.2615(7)	0.2767(4)	0.0407(3)	0.0837
C(32)	−0.2764(7)	0.0812(4)	0.1941(4)	0.0511
O(32)	−0.3132(7)	0.0127(4)	0.1940(3)	0.0816
C(41)	−0.3846(7)	0.2445(4)	0.2391(3)	0.0472
O(41)	−0.4985(5)	0.2527(3)	0.2381(3)	0.0632
C(42)	−0.3789(7)	0.2402(5)	0.3791(4)	0.0537
O(42)	0.0660(6)	0.4870(4)	0.2397(3)	0.0748
C(43)	−0.2784(7)	0.3861(4)	0.2808(4)	0.0504
O(43)	−0.3033(6)	0.4583(3)	0.2840(4)	0.0797
C(1)	−0.1332(5)	0.1653(3)	0.2907(3)	0.0350
C(2)	−0.0466(5)	0.2401(3)	0.2869(3)	0.0352
C(111)	−0.1690(5)	0.0826(3)	0.3517(3)	0.0353
C(112)	−0.3017(6)	0.0437(4)	0.3735(3)	0.0454
C(113)	−0.3364(7)	−0.0332(4)	0.4294(4)	0.0519
C(114)	−0.2385(8)	−0.0745(4)	0.4635(3)	0.0540
C(115)	−0.1061(7)	−0.0381(4)	0.4431(3)	0.0481
C(116)	−0.0717(6)	0.0411(4)	0.3880(3)	0.0408
C(211)	0.0172(6)	0.2547(3)	0.3443(3)	0.0388
C(212)	0.1590(6)	0.2641(4)	0.3301(3)	0.0527
C(213)	0.2209(7)	0.2802(5)	0.3810(4)	0.0625
C(214)	0.1435(8)	0.2894(4)	0.4467(4)	0.0584
C(215)	0.0036(8)	0.2783(5)	0.4628(4)	0.0668
C(216)	−0.0600(7)	0.2612(5)	0.4120(4)	0.0602
N(1)	0.5712(5)	0.2611(3)	−0.2406(3)	0.0494
P(1)	0.5460(2)	0.26025(9)	−0.31623(7)	0.0370
C(311)	0.6102(6)	0.1592(4)	−0.3400(3)	0.0421
C(312)	0.6705(7)	0.1582(4)	−0.4125(3)	0.0544
C(313)	0.7098(7)	0.0772(5)	−0.4287(4)	0.0591
C(314)	0.6890(7)	−0.0000(5)	−0.3743(5)	0.0596
C(315)	0.6302(8)	−0.0004(4)	−0.3029(4)	0.0614
C(316)	0.5936(7)	0.0802(4)	−0.2856(3)	0.0524
C(321)	0.3692(6)	0.2665(4)	−0.3205(3)	0.0406
C(322)	0.2954(7)	0.3419(4)	−0.3093(4)	0.0557
C(323)	0.1570(8)	0.3470(5)	−0.3085(4)	0.0680

Table 3 (continued)

Atom	x	y	z	U_{eq}
C(324)	0.0900(8)	0.2782(6)	−0.3190(5)	0.0759
C(325)	0.1615(8)	0.2025(6)	−0.3300(5)	0.0716
C(326)	0.2999(7)	0.1963(4)	−0.3300(5)	0.0568
C(331)	0.6377(7)	0.3541(4)	−0.3865(3)	0.0487
C(332)	0.7428(7)	0.3982(5)	−0.3736(4)	0.0643
C(333)	0.8146(9)	0.4692(6)	−0.4276(6)	0.0816
C(334)	0.784(1)	0.4953(6)	−0.4932(6)	0.0934
C(335)	0.680(1)	0.4524(6)	−0.5068(4)	0.0838
C(336)	0.6053(8)	0.3815(5)	−0.4532(4)	0.0650
P(2)	0.5072(2)	0.26719(9)	−0.16022(8)	0.0387
C(411)	0.3237(6)	0.2559(4)	−0.1324(3)	0.0447
C(412)	0.2602(7)	0.1793(4)	−0.1365(4)	0.0558
C(413)	0.1192(8)	0.1718(5)	−0.1209(4)	0.0720
C(414)	0.0381(8)	0.2358(6)	−0.0993(4)	0.0765
C(415)	0.0975(8)	0.3128(6)	−0.0955(4)	0.0744
C(416)	0.2402(7)	0.3235(5)	−0.1113(4)	0.0591
C(421)	0.5528(6)	0.3728(4)	−0.1493(3)	0.0406
C(422)	0.5868(8)	0.3805(5)	−0.0870(4)	0.0651
C(423)	0.613(1)	0.4640(6)	−0.0792(5)	0.0707
C(424)	0.6044(8)	0.5388(5)	−0.1325(5)	0.0675
C(425)	0.5737(8)	0.5318(4)	−0.1942(5)	0.0663
C(426)	0.5486(7)	0.4483(4)	−0.2038(4)	0.0526
C(431)	0.5766(7)	0.1791(4)	−0.1000(3)	0.0451
C(432)	0.6973(7)	0.1387(4)	−0.1274(4)	0.0598
C(433)	0.7521(8)	0.0737(5)	−0.0793(5)	0.0665
C(434)	0.6909(9)	0.0517(5)	−0.0064(5)	0.0713
C(435)	0.5705(9)	0.0905(5)	0.0208(4)	0.0693
C(436)	0.5116(8)	0.1551(4)	−0.0262(3)	0.0581

solution darkened to deep red. The reaction was monitored by examination of the ν(CO) region of the IR spectrum and when it was thought to be complete, the solution was evaporated and the residue dissolved in diethyl ether. The solvent was allowed to evaporate slowly to give purple-red crystals of $[\mathrm{CoRu_3(CO)_{11}}\{\mu_4\text{-}\eta^2\mathrm{C_2(C_6H_5)_2}\}][\mathrm{PPN}]$ (II) (160 mg, 0.115 mmol, 70% yield).

IR ν(CO): 2062m, 2025s, 1990s, 1980s, 1960m, 1950m, 1922m, 1915m, 1830s, 1816m cm^{1}. (Found: C, 52.3; H, 2.5. $\mathrm{C_{61}H_{40}NO_{11}P_2CoRu_3}$ calcd.: C, 52.8; H, 2.91%). ^{13}C NMR: ($\mathrm{CdCl_3}$, 500 MHz): 124.7, 126.3, 126.4, 127.3 128.7, 129.6, 132, 133.9 (s, C aromatic); 157.6 (s, C≡C); 179.1 (s, C≡C); 206 (m, CO).

Crystallography

Crystal data: $\mathrm{C_{61}H_{40}NO_{11}P_2CoRu_3}$, $M = 1387.1$, triclinic, space group $P\bar{1}$, a 9.9840(8), b 15.462(2), c 19.572(3) Å, α 75.08(1)°, β 75.15(1)°, γ 87.85(3)°, V 2821(1) Å^3, D_c 1.63 g cm^{-3} for $Z = 2$, λ(Mo-K_α) 0.71069, μ(Mo-K_α) 11.9 cm^{-1}. Crystal size: 0.3 × 0.3 × 0.1 mm. Data: 8485 reflexions were collected at room temperature (20 °C) in the range $3 < 2\theta < 46°$ on an Enraf–Nonius CAD4 diffractometer; 5622 reflexions with $I > 2\sigma(I)$ were used in subsequent calculations. An empirical absorption correction was applied [18]. (The corrections ranged from 1.00 to 1.26).

Table 4

Interatomic distances (Å) and bond angles (°). E.s.d.s in parentheses refer to the last significant digit.

Ru(1)–Ru(3)	2.6679(7)	Ru(3)–Co(4)	2.5923(8)
Ru(1)–Ru(2)	2.8165(6)	Ru(2)–Ru(3)	2.8118(6)
Ru(1)–C(11)	1.859(8)	Ru(3)–C(13)	2.194(7)
Ru(1)–C(12)	1.853(7)	Ru(3)–C(31)	1.888(7)
Ru(1)–C(13)	1.942(7)	Ru(3)–C(32)	1.873(6)
Ru(1)–C(1)	2.236(5)	Ru(3)–C(41)	2.092(7)
Ru(1)–C(2)	2.287(5)	Ru(3)–C(1)	2.247(5)
Ru(2)–Co(4)	2.5833(9)	Co(4)–C(41)	1.926(6)
Ru(2)–C(21)	1.923(8)	Co(4)–C(42)	1.761(8)
Ru(2)–C(22)	1.925(7)	Co(4)–C(43)	1.730(6)
Ru(2)–C(23)	1.893(8)	Co(4)–C(1)	2.048(5)
Ru(2)–C(2)	2.141(5)	Co(4)–C(2)	2.161(5)
C(1)–C(2)	1.445(7)	C(1)–C(111)	1.489(7)
C(2)–C(211)	1.493(7)	O(42)–C(42)	1.146(8)
C(11)–O(11)	1.155(8)	C(23)–O(23)	1.143(8)
C(12)–O(12)	1.148(8)	C(31)–O(31)	1.126(8)
C(13)–O(13)	1.166(7)	C(32)–O(32)	1.134(7)
C(21)–O(21)	1.135(8)	C(41)–O(41)	1.144(7)
C(22)–O(22)	1.130(8)	C(43)–O(43)	1.148(7)
Ru(1)–Co(4)	3.7625(8)	Ru(2)–C(43)	2.740(7)
C(11)–Ru(1)–Ru(3)	149.4(2)	Co(4)–Ru(3)–Ru(1)	91.32(2)
C(12)–Ru(1)–Ru(3)	110.9(2)	C(13)–Ru(3)–Co(4)	136.1(2)
C(12)–Ru(1)–C(11)	87.9(3)	C(1)–Ru(3)–C(13)	96.4(2)
C(13)–Ru(1)–Ru(3)	54.1(2)	C(1)–Ru(3)–C(31)	166.1(2)
C(13)–Ru(1)–C(11)	103.7(3)	C(1)–Ru(3)–C(32)	100.6(2)
C(13)–Ru(1)–C(12)	91.0(3)	C(1)–Ru(3)–C(41)	89.0(2)
C(21)–Ru(2)–Co(4)	97.9(3)	Ru(3)–Co(4)–Ru(2)	65.81(2)
C(22)–Ru(2)–Co(4)	105.3(2)	C(41)–Co(4)–Ru(2)	102.2(2)
C(22)–Ru(2)–C(21)	97.8(3)	C(41)–Co(4)–Ru(3)	52.7(2)
C(23)–Ru(2)–C(21)	88.8(3)	C(42)–Co(4)–Ru(2)	161.4(2)
C(23)–Ru(2)–C(22)	95.8(3)	C(23)–Ru(2)–Co(4)	156.7(2)
C(43)–Ru(2)–C(21)	76.3(3)	C(42)–Co(4)–Ru(3)	130.6(2)
C(43)–Ru(2)–C(22)	77.9(2)	C(42)–Co(4)–C(41)	95.8(3)
C(43)–Ru(2)–C(23)	162.7(3)	C(43)–Co(4)–Ru(2)	76.0(2)
C(2)–Ru(2)–Co(4)	53.5(1)	C(43)–Co(4)–Ru(3)	124.5(2)
C(2)–Ru(2)–C(21)	151.2(3)	C(43)–Co(4)–C(41)	102.3(3)
C(2)–Ru(2)–C(22)	93.2(2)	C(43)–Co(4)–C(42)	96.2(3)
C(2)–Ru(2)–C(23)	116.6(3)	Ru(3)–C(13)–Ru(1)	80.1(2)
C(2)–Ru(2)–C(43)	80.2(2)	Co(4)–C(41)–Ru(3)	80.3(3)
C(31)–Ru(3)–Ru(1)	122.2(2)	O(11)–C(11)–Ru(1)	177.3(7)
C(31)–Ru(3)–Co(4)	122.0(2)	O(12)–C(12)–Ru(1)	175.3(6)
C(31)–Ru(3)–C(13)	84.4(3)	O(13)–C(13)–Ru(1)	144.6(6)
C(32)–Ru(3)–Ru(1)	106.5(2)	O(13)–C(13)–Ru(3)	135.1(6)
C(32)–Ru(3)–Co(4)	123.0(2)	O(21)–C(21)–Ru(2)	178.1(7)
C(32)–Ru(3)–C(13)	85.2(3)	O(22)–C(22)–Ru(2)	179.1(6)
C(32)–Ru(3)–C(31)	93.3(3)	O(23)–C(23)–Ru(2)	171.6(6)
C(41)–Ru(3)–Ru(1)	138.2(2)	O(31)–C(31)–Ru(3)	178.9(7)
C(41)–Ru(3)–C(13)	174.0(2)	O(32)–C(32)–Ru(3)	174.4(6)
C(41)–Ru(3)–C(31)	89.8(3)	O(41)–C(41)–Ru(3)	140.9(5)
C(41)–Ru(3)–C(32)	96.5(3)	O(41)–C(41)–Co(4)	138.9(5)
C(1)–Ru(3)–Ru(1)	53.3(1)	O(42)–C(42)–Co(4)	176.2(6)
C(1)–Ru(3)–Co(4)	49.4(1)	O(43)–C(43)–Co(4)	169.3(7)
C(2)–C(1)–Ru(3)	108.0(3)	C(1)–C(2)–Ru(2)	108.1(3)
C(111)–C(1)–Ru(3)	125.4(4)	C(211)–C(2)–Ru(2)	123.2(4)
C(111)–C(1)–C(2)	126.6(5)	C(211)–C(2)–C(1)	128.1(5)

Computations were performed with the CRYSTALS system [19] adapted for a VAX 11/725. Atomic scattering factors for neutral Ru, Co, C, O and H were taken from ref. 20.

Structural determination. The use of direct methods (MULTAN [21]) gave the ruthenium and cobalt positions. All remaining non-hydrogen atoms were found by successive electron density maps. The hydrogen atoms were placed in calculated positions (C–H, 1.05 Å) with a fixed overall isotropic thermal parameter ($U = 0.06$). The coordinates of these H atoms were not refined, but were recalculated after each cycle. The structure was refined by least-squares techniques with all non-hydrogen atoms anisotropic, and with approximation (in four blocks) to the normal matrix, to $R = 0.0390$, $R_w = 0.044$ where $w = 1/\Sigma^{n}_{r=1} ArTr(x)[1 - (\Delta F/6\sigma(F_0))^2]^2$ with 3 coefficients, Ar, 4.584, −1.616, 3.123, for the Chebyshev polynomial $ArTr(x)$ where x was $F_c/F_c(\text{max})$ [22]. For a satisfactory, completed analysis the criteria were: a value of the r.m.s. (shift/e.s.d.) of 0.004 and the absence of significant features in the final difference map.

The atomic coordinates are listed in Table 3 and important bond distances and bond angles in Table 4. Copies of the observed structure amplitudes and calculated structure factors, atomic coordinates for H atoms, anisotropic thermal parameters for all atoms and a table of interatomic distances and bond angles for the PPN cation are available from the authors.

References

1 J.C. Daran, E. Cabrera, M.I. Bruce and M.L. Williams, J. Organomet. Chem., 319 (1987) 239.
2 M.I. Bruce, M.L. Williams, J.M. Patrick and A.H. White, J. Chem. Soc., Dalton Trans., (1985) 1229.
3 J.C. Daran, O. Kristiansson and Y. Jeannin, C.R. Acad. Sci. Paris, 300 (1985) 943.
4 M.I. Bruce, B.W. Skelton, A.H. White and M.L. Williams, J. Chem. Soc., Chem. Comm., (1985) 744.
5 M.I. Bruce and M.L. Williams, J. Organomet. Chem., 282 (1985) C11.
6 M.I. Bruce, M.R. Snow, E.R.T. Tiekink and M.L. Williams, J. Chem. Soc., Chem. Comm., (1986) 701.
7 L.F. Dahl and D.L. Smith, J. Am. Chem. Soc., 84 (1982) 2450.
8 P. Braunstein, J. Rose and O. Bars, J. Organomet. Chem., 252 (1983) C101.
9 E. Roland and H. Vahrenkamp, Organometallics, 2 (1983) 183.
10 B.F.G. Johnson, J. Lewis, B.E. Reichert, K.T. Schorpp and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1977) 1417.
11 K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 67.
12 J.R. Fox, W.L. Gladfelter, G.L. Geoffroy, I. Tavanaiepour, S. Abdel-Mequid and V.W. Day, Inorg. Chem., 20 (1981) 3230.
13 E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev., 83 (1983) 203.
14 A.J. Carty, Pure Appl. Chem., 54 (1982) 113.
15 J.C. Daran, Y. Jeannin and O. Kristiansson, Organometallics, 4 (1985) 1882.
16 J.K. Ruff and W.J. Schlientz, Inorg. Synth., 15 (1974) 87.
17 G.L. Geoffroy, J.R. Fox, E. Burkhardt, H.C. Foley, A.D. Harley and R. Rosen, Inorg. synth., 21 (1982) 61.
18 A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Cryst., (1968) 351.
19 J.R. Carruthers and D.J. Watkin, CRYSTALS, An Advanced Crystallographic Computer program, 1985, Chemical Crystallography Laboratory, Univ. of Oxford, England.
20 International Tables for X-ray Crystallography, Vol IV, 1974, Kynoch Press, Birmingham, England.
21 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declerq and M.M. Woolfson, 1984. MULTAN84. A system of Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Univ. of York, England.
22 E. Prince, Mathematical Techniques in Crystallography, (1982), Springer-Verlag, Berlin.