

Structure of a Ruthenium Complex Containing the Tricyanomethanide Anion as Ligand: [Ru{C(CN)₃}₃{P(C₆H₅)₃}₂(η -C₅H₅)]

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Abstract. [(η^5 -Cyclopentadienyl)tricyanomethanido-bis(triphenylphosphine)ruthenium(II)]-dichloromethane (1/1), $M_r = 865.74$, monoclinic, $P2_1/n$, $a = 11.263$ (3), $b = 16.274$ (4), $c = 22.165$ (4) Å, $\beta = 96.23$ (2)°, $V = 4038.8$ (18) Å³, $Z = 4$, $D_x = 1.42$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 6.3$ cm⁻¹, $F(000) = 1768$, $T = 293$ K. Least-squares refinement of 2671 unique observed [$|I| > 1.5\sigma(|I|)$] reflections gave $R = 0.060$. The crystal structure consists of discrete [Ru{C(CN)₃}₃{P(C₆H₅)₃}₂(η -C₅H₅) and CH₂-Cl₂ molecules with 6-coordinate ruthenium. The tricyanomethanide anion ligand coordinates through one of the N atoms rather than the central C atom [Ru–N 2.072 (5) Å]. The tricyanomethanide ion is nearly trigonal planar [average C–C bond length = 1.40 (1), average C–N bond length = 1.137 (9) Å, average C–C(4)–C bond angle = 120 (4)°]. The methylene chloride solvate molecule is found in the cavity formed by the propeller-like triphenylphosphine ligands.

Introduction. There has been continued interest in using the cyanocarbons and cyanocarbanions as ligands in transition-metal complexes (Baddley, 1968; Köhler, 1973). Tetracyanoethylene (tcne), in its neutral, mono- and dianion forms, has been shown to be capable of coordinating either *via* an electron pair of the central olefin bond (Ricci & Ibers, 1971; Panattoni, Bombieri, Belluco & Baddley, 1968) or *via* a nitrile (cyano) nitrogen (Rettig & Wing, 1969). In addition, the 1,1,2,3,3-pentacyanopropenide (pcp) anion has been demonstrated to coordinate to a metal ion *via* a cyano nitrogen (Bruce, Wallis, Skelton & White, 1981) or to act as a simple counterion (Sim, Woodhouse & Knox, 1979; Miller, Calabrese, Rommelmann, Chitipeddi, Zhang, Reiff & Epstein, 1987). Crystal structures of two simple alkali-metal salts, as well as the ammonium, silver(I) and copper(II) salts, of the tricyanomethanide ion (tcm) have been determined. In all five cases, coordination of the tcm anion to the cation is monodentate and occurs through the N atom. In these salts, each N atom of the tcm ion is coordinated to a different cation creating an infinite two- or three-dimensional network. The coordination of N atoms about the cation in the Na salt is found to

be nearly octahedral (Andersen, Klewe & Thom, 1967); in both the NH₄ and K salts the cations are 7-coordinate (Desiderato & Sass, 1965; Witt & Britton, 1971). The crystal structure of AgC(CN)₃ consists of double layers of 3-coordinate Ag^I ions (Konnert & Britton, 1966). In this structure the quasi-planar tcm ions form sheets in which the Ag^I ions are found. Two tcm ions in the sheet and one tcm ion from a neighboring sheet coordinate to the Ag^I ion, resulting in the double-layer structure. In the Cu^{II} salt the tcm ions form sheets which intersect at an angle of 79°. The 6-coordinate Cu^{II} ions are found at the intersections of the sheets in pseudo-octahedral holes (Biondi, Bonamico, Torelli & Vaciago, 1965).

N-coordination is expected in those crystals in which ionic interactions are predominant; however, the question has often been posed as to whether the tcm ion would coordinate *via* a cyano N or, assuming sp^3 hybridization, *via* the central C to the metal center of an isolated organometallic molecule (Beck, Hieber & Neumair, 1966; Lenarda & Baddley, 1972; Köhler, Hartung & Seifert, 1966). The latter type of complexation has been demonstrated for the analogous CH(CN)₂⁻ ion (Bailey, Higson & McKenzie, 1971; Cummins, Higson & McKenzie, 1973). For tcm itself, spectroscopic data have been shown to be consistent with N-coordination in the case of [P(C₆H₅)₃]₂Ir(CO)[C(CN)₃] and C-coordination for [P(C₆H₅)₃]₂PtH[C(CN)₃] (Beck, Schorpp, Oetker, Schlodder & Smedal, 1973). However, no crystallographic data have been reported for organometallic complexes containing the tcm ion. An X-ray structure determination of [Ru(tcm){P(C₆H₅)₃}₂(η -C₅H₅)]·CH₂Cl₂ was therefore undertaken.

Experimental. Yellow crystals of the dichloromethane solvate of [Ru(tcm){P(C₆H₅)₃}₂(η -C₅H₅)] were obtained as previously described (Bruce, Wallis, Skelton & White, 1981). A thin platelet, 0.05 × 0.16 × 0.19 mm, was mounted on a Syntex P2₁ diffractometer with a graphite monochromator, upgraded to Nicolet P3F specifications. Cell constants from 23 reflections in the range 12 < 2 θ < 23° (Campana, Shepherd & Litchman, 1981). A total of 4378 reflections measured

by ω scans, $2 \leq 2\theta \leq 40^\circ$, $[(\sin\theta)/\lambda]_{\max} = 0.4813 \text{ \AA}^{-1}$, $h: 0 \rightarrow 11$, $k: 0 \rightarrow 16$, $l: -22 \rightarrow 22$; 3753 unique, 2671 observed [$|I| < 1.5\sigma(|I|)$], $R_{\text{int}} = 0.024$. Scan speeds ranged from 2.50 to 29.30° min⁻¹, with a 1.0° scan range. Three check reflections (012, 004, 015) measured every 100 reflections, variations within counting statistics. Empirical (ψ -scan) absorption correction assuming an ellipsoidal crystal, $\mu = 6.3 \text{ cm}^{-1}$, $T_{\min} = 0.810$, $T_{\max} = 0.861$; Lorentz and polarization corrections.

Programs were contained in the *SHELXTL* package (Sheldrick, 1985) and scattering factors were obtained from *International Tables for X-ray Crystallography* (1974). Structure solved by direct methods and refined by a blocked-cascade least-squares method. Function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F) + gF^2]^{-1}$, g refined to zero. Ru and P atoms were identified from the E map calculated from direct methods. Positions of the remaining non-hydrogen atoms were identified from subsequent electron-density difference maps. The CH_2Cl_2 solvate molecule was found to be disordered. Refined site occupancy factors gave 0.543 (14) for one orientation [Cl(1) and Cl(2), anisotropic thermal parameters], and 0.457 (14) for the second orientation [Cl(1A) and Cl(2A), isotropic thermal parameters]. Refinement of the structure continued with the following conditions: anisotropic thermal parameters for all other non-hydrogen atoms; common H isotropic thermal parameter [0.087 (5) Å²]; C—H distances in $\eta\text{-C}_5\text{H}_5$ and CH_2Cl_2 restricted to 0.96 Å; H—C—H angles of 109.5° for CH_2Cl_2 ; phenyl groups held rigid with C—C distance of 1.395 Å, C—H distances of 0.96 Å, and C—C—C and C—C—H angles of 120°. Final refinement of 425 least-squares parameters gave $R = 0.060$, $wR = 0.041$, goodness of fit = 1.45, and $(\Delta/\sigma)_{\max} = 0.055$. Excursions in final electron-density difference map ranged from -0.5 to 0.5 e \AA^{-3} [near Cl(2)]. $R = 0.091$ and $wR = 0.041$ for all 3753 reflections. Non-hydrogen atomic coordinates are presented in Table 1 and selected bond lengths and angles in Table 2.*

Discussion. The complex crystallizes as discrete [Ru-{C(CN)₃}{P(C₆H₅)₃}₂($\eta\text{-C}_5\text{H}_5$)] units with CH_2Cl_2 solvate molecules incorporated in the structure. An *ORTEP* diagram (Johnson, 1965) of the moiety viewed approximately down the Ru—cyclopentadienide (Cp) axis is shown in Fig. 1. In addition to the bulky triphenylphosphine ligands, the Ru^{II} center is coordinated by the Cp and tcm ligands, each of which has a

* Lists of observed and calculated structure factors, anisotropic thermal parameters, H-atom coordinates and a stereographic packing diagram of the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51073 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U/U_{eq}
Ru	-1658 (1)	1374 (1)	3764 (1)	32 (1)*
C(1)	-4344 (7)	1189 (5)	4092 (3)	38 (3)*
C(2)	-5939 (8)	797 (5)	4727 (4)	56 (4)*
C(3)	-6392 (9)	1236 (9)	3681 (5)	93 (6)*
C(4)	-5538 (8)	1076 (5)	4178 (4)	52 (4)*
N(1)	-3399 (5)	1303 (4)	3979 (3)	37 (2)*
N(2)	-6283 (7)	586 (5)	5159 (3)	85 (4)*
N(3)	-7112 (9)	1349 (11)	3281 (4)	170 (7)*
C(5)	183 (8)	905 (5)	3718 (4)	44 (4)*
C(6)	-549 (8)	666 (5)	3182 (4)	44 (4)*
C(7)	-1448 (8)	144 (5)	3359 (4)	54 (4)*
C(8)	-1289 (7)	62 (5)	4001 (3)	45 (4)*
C(9)	-300 (7)	526 (5)	4216 (4)	44 (4)*
P(1)	-2312 (2)	2196 (1)	2933 (1)	36 (1)*
C(12)	-2774 (5)	1597 (3)	1717 (3)	47 (4)*
C(13)	-3346	1085	1272	63 (4)*
C(14)	-4174	506	1427	64 (5)*
C(15)	-4430	438	2026	62 (5)*
C(16)	-3858	950	2472	54 (4)*
C(11)	-3029	1530	2317	35 (4)*
C(22)	-4667 (7)	2759 (4)	2999 (2)	53 (4)*
C(23)	-5525	3355	3081	64 (5)*
C(24)	-5183	4171	3182	69 (5)*
C(25)	-3983	4392	3200	69 (5)*
C(26)	-3125	3797	3118	45 (4)*
C(21)	-3466	2980	3017	33 (4)*
C(32)	-1642 (4)	3327 (4)	2066 (3)	48 (4)*
C(33)	-819	3760	1762	67 (5)*
C(34)	403	3656	1927	76 (5)*
C(35)	801	3119	2396	57 (4)*
C(36)	-21	2685	2700	50 (4)*
C(31)	-1243	2789	2535	36 (4)*
P(2)	-1164 (2)	2326 (1)	4534 (1)	36 (1)*
C(42)	-697 (5)	2315 (3)	5804 (3)	58 (4)*
C(43)	-755	1999	6385	68 (5)*
C(44)	-1371	1770	6462	60 (5)*
C(45)	-1929	855	5958	59 (4)*
C(46)	-1870	1171	5376	37 (4)*
C(41)	-1254	1900	5299	37 (4)*
C(52)	-1343 (4)	4002 (4)	4869 (3)	42 (4)*
C(53)	-1983	4707	4990	59 (5)*
C(54)	-3226	4709	4885	58 (5)*
C(55)	-3831	4007	4659	61 (4)*
C(56)	-3191	3302	4538	48 (4)*
C(51)	-1947	3300	4643	30 (3)*
C(62)	648 (7)	3237 (4)	4121 (3)	53 (4)*
C(63)	1826	3474	4078	84 (6)*
C(64)	2753	3124	4462	105 (7)*
C(65)	2502	2537	4888	98 (7)*
C(66)	1324	2300	4931	67 (5)*
C(61)	397	2650	4547	43 (4)*
Cl(1)	-2543 (10)	9044 (8)	8361 (6)	214 (7)*
Cl(2)	-141 (7)	8432 (8)	8870 (5)	284 (7)*
C(70)	-1528 (11)	8285 (8)	8772 (6)	138 (7)*
Cl(1A)	-2095 (7)	8711 (5)	8145 (3)	121 (4)*
Cl(2A)	-17 (6)	8611 (5)	8939 (3)	104 (2)

* U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

formal charge of -1 . The Ru is 6-coordinate, with the $\eta\text{-C}_5\text{H}_5$ ligand formally occupying three positions, as seen for the analogous $\text{Ru}(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)\text{X}$ ($\text{X} = \text{halide}$ or pseudo-halide) complexes of Bruce and co-workers (Bruce, Wallis, Skelton & White, 1981; Bruce, Wong, Skelton & White, 1981). The structure of the $\text{P}(\text{C}_6\text{H}_5)_3$ ligands is very similar to that described in the analogous complexes. The tcm ligand is seen to coordinate through one of the nitrogens as has often been suggested. Its coordination to Ru is best described as a pseudo-halide anion acting as a hard σ -base (Rettig & Wing, 1969). There is very little *trans* effect on the Cp ring as the carbons most nearly opposite N(1) have Ru—C bond lengths very similar to those opposite P(1) and P(2). The Ru—C bond lengths range from

where C-coordination has been confirmed (Bailey, Higson & McKenzie, 1971), and the Pt complex of $C(CN)_3^-$ where C-coordination has been assigned spectroscopically, the coordination sphere about the metal is not as crowded (fewer ligands) and thus may permit a different ligand coordination scheme.

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trans-Dichlorobis(di-*n*-propyl sulfoxide)platinum(II)

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Abstract. $[PtCl_2(C_6H_{14}OS)_2]$, $M_r = 534.48$, monoclinic, $P2_1/c$, $a = 9.092$ (2), $b = 5.696$ (2), $c = 19.749$ (7) Å, $\beta = 110.63$ (3)°, $V = 957.2$ (6) Å³, $Z = 2$, $D_x = 1.854$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu(Mo K\alpha) = 7.894$ mm⁻¹, $F(000) = 520$, room temperature, $R = 0.047$ for 1842 unique observed reflections. The Pt atom is located on a center of symmetry. Pt has *trans* square-planar coordination and the sulfoxide ligands are bonded through their S atoms. The Pt–Cl bond distances are 2.292 (3) Å. The Pt–S bond lengths [2.292 (2) Å] are significantly longer than the corresponding distances in the *cis* isomer. The packing consists of layers of molecules parallel to the *ab* plane.

Introduction. When K_2PtCl_4 reacts with sulfoxide ligands (*L*) in water, *trans*-[Pt(*L*)₂Cl₂] is first formed

because of the large *trans* effect of sulfoxides. The compound is then isomerized to the *cis*-isomer since the enhanced $\pi(d-d)$ bonding seems to be quite efficient in *cis* Pt compounds (Price, Williamson, Schramm & Wayland, 1972; Price, Birk & Wayland, 1978). *cis* structures have been reported for all the Pt^{II} disubstituted complexes except with a very sterically demanding ligand, diisoamyl sulfoxide, which gave only the *trans* isomer (Price *et al.*, 1972). With Me₂SO the *trans* compound cannot be isolated. But with more bulky ligands like benzyl methyl sulfoxide (bmso) the *trans* compound has been isolated (Rochon, Kong & Girard, 1986). The two isomers can be identified by their stretching $\nu(Pt-Cl)$. For example *cis*-[Pt(bmso)₂Cl₂] absorbs at 331 and 311 cm⁻¹ while the *trans* isomer shows only one band at 349 cm⁻¹. The colors of the two isomers are also quite different. The *cis*