# Structure of a Ruthenium Complex Containing the Tricyanomethanide Anion as Ligand: $\left[\mathbf{R u}\left\{\mathbf{C}(\mathbf{C N})_{3}\right\}\left\{\mathbf{P}\left(\mathbf{C}_{6} \mathbf{H}_{5}\right)_{3}\right\}_{2}\left(\eta-\mathbf{C}_{5} \mathbf{H}_{5}\right)\right]$ 

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#### Abstract

Cyclopentadienyl)tricyanomethanido-bis(triphenylphosphine)ruthenium(II)]-dichloromethane $(1 / 1), \quad M_{r}=865.74$, monoclinic, $P 22_{1} / n$, $a=11.263$ (3), $b=16.274$ (4), $c=22.165$ (4) $\AA, \beta$ $=96.23(2)^{\circ}, \quad V=4038.8(18) \AA^{3}, \quad Z=4, \quad D_{x}=$ $1.42 \mathrm{~g} \mathrm{~cm}^{-3}, \quad \lambda($ Mo $K \alpha)=0.71069 \AA, \quad \mu=6.3 \mathrm{~cm}^{-1}$, $F(000)=1768, T=293 \mathrm{~K}$. Least-squares refinement of 2671 unique observed $[|I|>1.5 \sigma(|I|)$ ] reflections gave $R=0.060$. The crystal structure consists of discrete $\left[\mathrm{Ru}\left\{\mathrm{C}(\mathrm{CN})_{3}\right\}\left\{\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right\}_{2}\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right)\right]$ and $\mathrm{CH}_{2}-$ $\mathrm{Cl}_{2}$ molecules with 6 -coordinate ruthenium. The tricyanomethanide anion ligand coordinates through one of the N atoms rather than the central C atom $[\mathrm{Ru}-\mathrm{N}$ $2.072(5) \AA]$. The tricyanomethanide ion is nearly trigonal planar [average $\mathrm{C}-\mathrm{C}$ bond length $=1.40$ (1), average $\mathrm{C}-\mathrm{N}$ bond length $=1 \cdot 137(9) \AA$, average $\mathrm{C}-\mathrm{C}(4)-\mathrm{C}$ bond angle $\left.=120(4)^{\circ}\right]$. 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, Chittipeddi, 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 $\mathrm{NH}_{4}$ and K salts the cations are 7-coordinate (Desiderato \& Sass, 1965; Witt \& Britton, 1971). The crystal structure of $\mathrm{AgC}(\mathrm{CN})_{3}$ consists of double layers of 3 -coordinate $\mathrm{Ag}^{1}$ ions (Konnert \& Britton, 1966). In this structure the quasi-planar tcm ions form sheets in which the $\mathrm{Ag}^{1}$ ions are found. Two tcm ions in the sheet and one tcm ion from a neighboring sheet coordinate to the $\mathrm{Ag}^{\mathrm{I}}$ ion, resulting in the double-layer structure. In the $\mathrm{Cu}^{11}$ salt the tem ions form sheets which intersect at an angle of $79^{\circ}$. The 6 -coordinate $\mathrm{Cu}^{1 \mathrm{I}}$ 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 tem ion would coordinate via a cyano N or, assuming $s p^{3}$ 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-$(\mathrm{CN})_{2}^{-}$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 $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right]_{2} \mathrm{Ir}$ (CO) $\left[\mathrm{C}(\mathrm{CN})_{3}\right]$ and C -coordination for $\left[\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right]_{2}$ $\mathrm{PtH}\left[\mathrm{C}(\mathrm{CN})_{3}\right]$ (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 $\left[\mathrm{Ru}(\mathrm{tcm})\left\{\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right\}_{2}\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right)\right] . \mathrm{CH}_{2} \mathrm{Cl}_{2}$ was therefore undertaken.

Experimental. Yellow crystals of the dichloromethane solvate of $\left[\mathrm{Ru}(\mathrm{tcm})\left\{\mathrm{P}_{\left.\left.\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right\}_{2}\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right)\right] \text { were ob- }}\right.\right.$ tained as previously described (Bruce, Wallis, Skelton \& White, 1981). A thin platelet, $0.05 \times 0.16 \times$ 0.19 mm , was mounted on a Syntex $P 2_{1}$ diffractometer with a graphite monochromator, upgraded to Nicolet $P 3 F$ specifications. Cell constants from 23 reflections in the range $12<2 \theta<23^{\circ}$ (Campana, Shepherd \& Litchman, 1981). A total of 4378 reflections measured
by $\omega$ scans, $2 \leq 2 \theta \leq 40^{\circ},[(\sin \theta) / \lambda]_{\max }=0.4813 \AA^{-1}$, $h: 0 \rightarrow 11, k: 0 \rightarrow 16, \quad l:-22 \rightarrow 22 ; 3753$ unique, 2671 observed $[|I|<1.5 \sigma(|I|)], R_{\text {int }}=0.024$. Scan speeds ranged from 2.50 to $29.30^{\circ} \mathrm{min}^{-1}$, with a $1.0^{\circ}$ scan range. Three check reflections $(01 \overline{2}, 00 \overline{4}, 015)$ measured every 100 reflections, variations within counting statistics. Empirical ( $\psi$-scan) absorption correction assuming an ellipsoidal crystal, $\mu=6.3 \mathrm{~cm}^{-1}, T_{\text {min }}$ $=0.810, \quad T_{\text {max }}=0.861$; 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 $\sum w\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2}, w=\left[\sigma^{2}(F)+g F^{2}\right]^{-1}$, $g$ 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solvate molecule was found to be disordered. Refined site occupancy factors gave 0.543 (14) for one orientation $[\mathrm{Cl}(1)$ and $\mathrm{Cl}(2)$, anisotropic thermal parameters], and 0.457 (14) for the second orientation $[\mathrm{Cl}(1 A)$ and $\mathrm{Cl}(2 A)$, 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 $\left[0.087(5) \AA^{2}\right] ; \mathrm{C}-\mathrm{H}$ distances in $\eta-\mathrm{C}_{5} \mathrm{H}_{5}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ restricted to $0.96 \AA ; \mathrm{H}-\mathrm{C}-\mathrm{H}$ angles of $109.5^{\circ}$ for $\mathrm{CH}_{2} \mathrm{Cl}_{2}$; phenyl groups held rigid with $\mathrm{C}-\mathrm{C}$ distance of $1.395 \AA, \mathrm{C}-\mathrm{H}$ distances of $0.96 \AA$, and $\mathrm{C}-\mathrm{C}-\mathrm{C}$ and $\mathrm{C}-\mathrm{C}-\mathrm{H}$ angles of $120^{\circ}$. Final refinement of 425 least-squares parameters gave $R=0.060, w R=0.041$, goodness of fit $=1.45$, and $(\Delta / \sigma)_{\text {max }}=0.055$. Excursions in final electron-density difference map ranged from -0.5 to $0.5 \mathrm{e} \AA^{-3}$ [near $\mathrm{Cl}(2)] . R=0.091$ and $w R=0.041$ 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 $\left\{\mathrm{C}(\mathrm{CN})_{3}\right\}\left\{\mathrm{P}_{\left.\left.\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}\right\}_{2}\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right)\right] \text { units with } \mathrm{CH}_{2} \mathrm{Cl}_{2}, ~}^{\text {and }}\right.$ solvate molecules incorporated in the structure. An ORTEP diagram (Johnson, 1965) of the moiety viewed approximately down the Ru-cyclopentadienide $(\mathrm{Cp})$ axis is shown in Fig. 1. In addition to the bulky triphenylphosphine ligands, the $\mathrm{Ru}^{11}$ center is coordinated by the Cp and tcm ligands, each of which has a

[^0]Table 1. Atomic coordinates $\left(\times 10^{4}\right)$ and isotropic thermal parameters $\left(\AA^{2} \times 10^{3}\right)$

|  | $\boldsymbol{x}$ | $y$ | $z$ | $U / U_{\text {eq }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 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 | 1.70 | 6462 | 60 (5)* |
| C(45) | -1929 | 855 | 5958 | 59 (4)* |
| C(46) | -1870 | 1171 | 5376 | 37 (4)* |
| $\mathrm{C}(41)$ | -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)* |
| $\mathrm{Cl}(1)$ | -2543 (10) | 9044 (8) | 8361 (6) | 214 (7)* |
| $\mathrm{Cl}(2)$ | -141(7) | 8432 (8) | 8870 (5) | 284 (7)* |
| C (70) | -1528(11) | 8285 (8) | 8772 (6) | 138 (7)* |
| $\mathrm{Cl}(1 A)$ | -2095 (7) | 8711 (5) | 8145 (3) | 121 (4) |
| $\mathrm{Cl}(2 A)$ | -17(6) | 8611 (5) | 8939 (3) | 104 (2) |

formal charge of -1 . The Ru is 6 -coordinate, with the $\eta-\mathrm{C}_{5} \mathrm{H}_{5}$ ligand formally occupying three positions, as seen for the analogous $\operatorname{Ru}\left(\mathrm{PR}_{3}\right)_{2}\left(\eta-\mathrm{C}_{5} \mathrm{H}_{5}\right) X(X=$ halide or pseudo-halide) complexes of Bruce and co-workers (Bruce, Wallis, Skelton \& White, 1981; Bruce, Wong, Skelton \& White, 1981). The structure of the $\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}$ ligands is very similar to that described in the analogous complexes. The tem 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 $\sigma$-base (Rettig \& Wing, 1969). There is very little trans effect on the Cp ring as the carbons most nearly opposite $\mathrm{N}(1)$ have $\mathrm{Ru}-\mathrm{C}$ bond lengths very similar to those opposite $\mathrm{P}(1)$ and $P(2)$. The $\mathrm{Ru}-\mathrm{C}$ bond lengths range from

Table 2. Bond lengths $(\AA)$ and bond angles $\left({ }^{\circ}\right)$

| $\mathrm{Ru}-\mathrm{N}(1)$ | 2.071 (6) | $\mathrm{C}(5)-\mathrm{C}(9)$ | 1.423 (13) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Ru}-\mathrm{C}(5)$ | 2.222 (9) | C (6)-C(7) | 1.411 (13) |
| $\mathrm{Ru}-\mathrm{C}(6)$ | 2.214 (10) | C (7)-C(8) | 1.422 (11) |
| $\mathrm{Ru}-\mathrm{C}(7)$ | $2 \cdot 217$ (9) | $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.386 (11) |
| $\mathrm{Ru}-\mathrm{C}(8)$ | 2.226 (8) | $\mathrm{P}(1)-\mathrm{C}(11)$ | 1.857 (6) |
| $\mathrm{Ru}-\mathrm{C}(9)$ | 2.217 (8) | $\mathrm{P}(1)-\mathrm{C}(21)$ | 1.846 (7) |
| $\mathrm{Ru}-\mathrm{P}(1)$ | 2.331 (3) | $\mathrm{P}(1)-\mathrm{C}(31)$ | 1.842 (7) |
| $\mathrm{Ru}-\mathrm{P}(2)$ | 2.327 (3) | $\mathrm{P}(2)-\mathrm{C}(41)$ | 1.846 (8) |
| $\mathrm{C}(1)-\mathrm{C}(4)$ | 1.391 (12) | $\mathrm{P}(2)-\mathrm{C}(51)$ | 1.844 (7) |
| $\mathrm{C}(1)-\mathrm{N}(1)$ | 1.135 (10) | $\mathrm{P}(2)-\mathrm{C}(61)$ | 1.832 (8) |
| $\mathrm{C}(2)-\mathrm{C}(4)$ | 1.416 (13) | $\mathrm{Cl}(\mathrm{I})-\mathrm{C}(70)$ | 1.853 (17) |
| $\mathrm{C}(2)-\mathrm{N}(2)$ | 1.127 (12) | $\mathrm{Cl}(2)-\mathrm{C}(70)$ | 1.572 (15) |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | 1.406 (13) | $\mathrm{C}(70)-\mathrm{Cl}(1 A)$ | 1.621 (14) |
| $\mathrm{C}(3)-\mathrm{N}(3)$ | 1.149 (14) | $\mathrm{C}(70)-\mathrm{Cl}(2 A)$ | 1.782 (14) |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | 1.424 (13) |  |  |
|  |  | $\mathrm{N}(1)-\mathrm{Ru}-\mathrm{C}(5)$ | 154.6 (3) |
| $\mathrm{Ru}-\mathrm{C}(6)-\mathrm{C}(7)$ | 71.6 (5) | $\mathrm{N}(1)-\mathrm{Ru}-\mathrm{C}(6)$ | 135.6 (3) |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | 107.4 (8) | $\mathrm{C}(5)-\mathrm{Ru}-\mathrm{C}(6)$ | 37.4 (3) |
| $\mathrm{Ru}-\mathrm{C}(7)-\mathrm{C}(6)$ | 71.3 (5) | $\mathrm{N}(1)-\mathrm{Ru}-\mathrm{C}(7)$ | 100.9 (3) |
| $\mathrm{Ru}-\mathrm{C}(7)-\mathrm{C}(8)$ | 71.7 (5) | $\mathrm{C}(5)-\mathrm{Ru}-\mathrm{C}(7)$ | 61.9 (3) |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | 108.6 (7) | $\mathrm{C}(6)-\mathrm{Ru}-\mathrm{C}(7)$ | 37.1 (3) |
| $\mathrm{Ru}-\mathrm{C}(8)-\mathrm{C}(7)$ | 71.0 (5) | $\mathrm{N}(1)-\mathrm{Ru}-\mathrm{C}(8)$ | 92.8 (3) |
| $\mathrm{Ru}-\mathrm{C}(8)-\mathrm{C}(9)$ | 71.4 (5) | $\mathrm{C}(5)-\mathrm{Ru}-\mathrm{C}(8)$ | 62.0 (3) |
| C (7)-C (8)-C(9) | 107.5 (7) | $\mathrm{C}(6)-\mathrm{Ru}-\mathrm{C}(8)$ | 62.4 (3) |
| $\mathrm{Ru}-\mathrm{C}(9)-\mathrm{C}(5)$ | 71.5 (5) | $\mathrm{C}(7)-\mathrm{Ru}-\mathrm{C}(8)$ | 37.3 (3) |
| $\mathrm{Ru}-\mathrm{C}(9)-\mathrm{C}(8)$ | 72.2 (5) | $\mathrm{N}(1)-\mathrm{Ru}-\mathrm{C}(9)$ | 119.1 (3) |
| $\mathrm{C}(5)-\mathrm{C}(9)-\mathrm{C}(8)$ | 109.3 (7) | $\mathrm{C}(5)-\mathrm{Ru}-\mathrm{C}(9)$ | 37.4 (3) |
| $\mathrm{Ru}-\mathrm{P}(1)-\mathrm{C}(11)$ | 108.7 (2) | $\mathrm{C}(6)-\mathrm{Ru}-\mathrm{C}(9)$ | 62.2 (3) |
| $\mathrm{Ru}-\mathrm{P}(1)-\mathrm{C}(21)$ | 118.9 (2) | $\mathrm{C}(7)-\mathrm{Ru}-\mathrm{C}(9)$ | 61.4 (3) |
| $\mathrm{C}(11)-\mathrm{P}(1)-\mathrm{C}(21)$ | 102.9 (3) | $\mathrm{C}(8)-\mathrm{Ru}-\mathrm{C}(9)$ | 36.4 (3) |
| $\mathrm{Ru}-\mathrm{P}(1)-\mathrm{C}(31)$ | $120 \cdot 8$ (2) | $\mathrm{N}(1)-\mathrm{Ru}-\mathrm{P}(1)$ | 89.3 (2) |
| $\mathrm{C}(11)-\mathrm{P}(1)-\mathrm{C}(31)$ | $102 \cdot 1$ (3) | $\mathrm{C}(5)-\mathrm{Ru}-\mathrm{P}(1)$ | $112 \cdot 1$ (3) |
| $\mathrm{C}(21)-\mathrm{P}(1)-\mathrm{C}(31)$ | 101.0 (3) | $\mathrm{C}(6)-\mathrm{Ru}-\mathrm{P}(1)$ | 89.3 (2) |
| $\mathrm{P}(1)-\mathrm{C}(11)-\mathrm{C}(12)$ | 122.4 (2) | $\mathrm{C}(7)-\mathrm{Ru}-\mathrm{P}(1)$ | 103.7 (2) |
| $\mathrm{P}(1)-\mathrm{C}(11)-\mathrm{C}(16)$ | 117.6 (2) | $\mathrm{C}(8)-\mathrm{Ru}-\mathrm{P}(1)$ | 140.5 (2) |
| $\mathrm{P}(1)-\mathrm{C}(21)-\mathrm{C}(22)$ | 120.6 (2) | $\mathrm{C}(9)-\mathrm{Ru}-\mathrm{P}(1)$ | 149.1 (2) |
| $\mathrm{P}(1)-\mathrm{C}(21)-\mathrm{C}(26)$ | 119.3 (2) | $\mathrm{N}(1)-\mathrm{Ru}-\mathrm{P}(2)$ | 91.4 (2) |
| $\mathrm{P}(1)-\mathrm{C}(31)-\mathrm{C}(32)$ | 120.7 (2) | $\mathrm{C}(5)-\mathrm{Ru}-\mathrm{P}(2)$ | 96.5 (2) |
| $\mathrm{P}(1)-\mathrm{C}(31)-\mathrm{C}(36)$ | 119.2 (2) | $\mathrm{C}(6)-\mathrm{Ru}-\mathrm{P}(2)$ | 131.9 (2) |
| $\mathrm{Ru}-\mathrm{P}(2)-\mathrm{C}(41)$ | 113.1 (2) | $\mathrm{C}(7)-\mathrm{Ru}-\mathrm{P}(2)$ | 150.5 (2) |
| $\mathrm{Ru}-\mathrm{P}(2)-\mathrm{C}(51)$ | 126.1 (2) | $\mathrm{C}(8)-\mathrm{Ru}-\mathrm{P}(2)$ | 116.2 (2) |
| $\mathrm{C}(41)-\mathrm{P}(2)-\mathrm{C}(51)$ | 97.3 (3) | $\mathrm{C}(9)-\mathrm{Ru}-\mathrm{P}(2)$ | 89.1 (2) |
| $\mathrm{Ru}-\mathrm{P}(2)-\mathrm{C}(61)$ | 110.9 (2) | $\mathrm{P}(1)-\mathrm{Ru}-\mathrm{P}(2)$ | 103.1 (1) |
| $\mathrm{C}(41)-\mathrm{P}(2)-\mathrm{C}(61)$ | 104.0 (3) | $\mathrm{C}(4)-\mathrm{C}(1)-\mathrm{N}(1)$ | 174.8 (8) |
| $\mathrm{C}(51)-\mathrm{P}(2)-\mathrm{C}(61)$ | 102.8 (3) | $\mathrm{C}(4)-\mathrm{C}(2)-\mathrm{N}(2)$ | 178.3 (10) |
| $\mathrm{P}(2)-\mathrm{C}(41)-\mathrm{C}(42)$ | 119.4 (2) | $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{N}(3)$ | 177.9 (13) |
| $\mathrm{P}(2)-\mathrm{C}(41)-\mathrm{C}(46)$ | 120.6 (2) | $\mathrm{C}(1)-\mathrm{C}(4)-\mathrm{C}(2)$ | 124.3 (7) |
| $\mathrm{P}(2)-\mathrm{C}(51)-\mathrm{C}(52)$ | 122.0 (2) | $\mathrm{C}(1)-\mathrm{C}(4)-\mathrm{C}(3)$ | 117.2 (8) |
| $\mathrm{P}(2)-\mathrm{C}(51)-\mathrm{C}(56)$ | 117.8 (2) | $\mathrm{C}(2)-\mathrm{C}(4)-\mathrm{C}(3)$ | 118.5 (8) |
| $\mathrm{P}(2)-\mathrm{C}(61)-\mathrm{C}(62)$ | 116.8 (2) | $\mathrm{Ru}-\mathrm{N}(1)-\mathrm{C}(1)$ | 173.7 (6) |
| $\mathrm{P}(2)-\mathrm{C}(61)-\mathrm{C}(66)$ | 123.1 (2) | $\mathrm{Ru}-\mathrm{C}(5)-\mathrm{C}(6)$ | 71.0 (5) |
| $\mathrm{Cl}(1)-\mathrm{C}(70)-\mathrm{Cl}(2)$ | 121.1 (10) | $\mathrm{Ru}-\mathrm{C}(5)-\mathrm{C}(9)$ | 71.1 (5) |
| $\mathrm{Cl}(1 A)-\mathrm{C}(70)-\mathrm{Cl}(2 A)$ | ) $109.2(8)$ | $\mathrm{C}(6)-\mathrm{C}(5)-\mathrm{C}(9)$ | 107.1 (7) |
|  |  | $\mathrm{Ru}-\mathrm{C}(6)-\mathrm{C}(5)$ | 71.6 (5) |



Fig. 1. View of the title complex.
1.389 (17) to 1.424 (23) $\AA$, with an average length of 1.413 (23) $\AA$. The $\mathrm{Ru}-\mathrm{N}(1)$ distance $[2.072(5) \AA$ ] is longer than in the analogous pentacyanopropenide (pcp) complex $[2.033$ (6) A] (Bruce, Wallis, Skelton \& White, 1981).

The orientation of the complex in the unit cell may be approximately derived by taking a complex with its Cp plane perpendicular to the $y$ axis and rotating it $37^{\circ}$ about an axis parallel to the $z$ axis and through the Ru ion (actual angles between the normal to the Cp least-squares plane and the $x, y$ and $z$ axes are 53,143 and $99^{\circ}$, respectively). In this orientation of the complex the plane of the tcm ion is approximately parallel to the $x z$ plane of the crystal (angles between the normal to the tcm least-squares plane and the $x, y$ and $z$ axes are 96,18 and $72^{\circ}$, respectively). The axis of the tcm ion [corresponding to a least-squares line through the $\mathrm{Ru}, \mathrm{N}(1), \mathrm{C}(1)$ and $\mathrm{C}(4)$ atoms] is nearly parallel to the $x$ axis. A phenyl ring on the complex one $a$-axis translation away fits into the bifurcation of the two non-coordinate cyano groups. The complexes are arranged in planes parallel to the $x z$ plane. Complexes in one set of alternating planes are oriented such that the $y$ coordinate of the Cp ring center is more positive than the $y$ coordinate of the Ru atom; thus the Cp ring lies above the Ru atom. The Cp rings in the complexes in the other planes lie below the Ru atoms.

The disordered methylene chloride solvent molecule fits into a cavity formed by the propeller-like triphenylphosphine ligands. The H atoms of the methylene chloride are directed into the space between two phenyl rings of the complex, distances ranging from 3.0 to $3.5 \AA$ between $\mathrm{H}(71)$ and the $\mathrm{C}(4 n)$ atoms and from 2.9 to $3.3 \AA$ between $\mathrm{H}(72)$ and the $\mathrm{C}(5 n)$ atoms. The Cl atoms are directed away from the complex and are bounded by the phenyl rings of surrounding complexes. There are also contacts between the Cl atoms and $\mathrm{H}(5)$ of the Cp ring and $\mathrm{N}(3)$ of the tem ion.

The tcm ion is very nearly trigonal planar, as was observed for both the Ktcm and Natcm structures (Witt \& Britton, 1971, Andersen, Klewe \& Thom, 1967). The $\mathrm{C}-\mathrm{C}$ bond lengths are similar at 1.389 (8), 1.41 (3) and 1.41 (3) $\AA$ for $\mathrm{C}(4)-\mathrm{C}(1), \mathrm{C}(4)-\mathrm{C}(2)$ and $\mathrm{C}(4)-\mathrm{C}(3)$, respectively. Furthermore, the sum of the angles about $\mathrm{C}(4)$ totals $360 \cdot 0^{\circ}$, indicating a strong $\pi$-bonding stabilization of the planar geometry for the anion (Hipps \& Aplin, 1985). Apparently any $\pi$ backbonding between $\mathrm{Ru}^{+}$and $\mathrm{C}(\mathrm{CN})_{3}^{-}$has little effect on the geometric parameters. The only significant distortion from trigonal-planar geometry is the $\mathrm{C}(4)-$ $\mathrm{C}(1)-\mathrm{N}(1)$ bond angle of $174.7(22)^{\circ}$, which is primarily in the plane of the anion and still within three standard deviations of $180^{\circ}$. As Fig. 1 suggests, this is in part due to the steric crowding of the $\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}$ ligands. This steric crowding may be a factor regarding coordination of tem through the N. It is interesting to note that in both the cobalt complex of $\mathrm{CH}(\mathrm{CN})_{2}^{-}$
where C-coordination has been confirmed (Bailey, Higson \& McKenzie, 1971), and the Pt complex of $\mathrm{C}(\mathrm{CN})_{3}$ 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. $\quad\left[\mathrm{PtCl}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{14} \mathrm{OS}\right)_{2}\right], \quad M_{r}=534.48$, monoclinic, $\quad P 2_{1} / c, \quad a=9.092$ (2), $\quad b=5.696$ (2), $\quad c=$ 19.749 (7) $\AA, \quad \beta=110.63$ (3) ${ }^{\circ}, \quad V=957.2$ (6) $\AA^{3}, \quad Z$ $=2, \quad D_{x}=1.854 \mathrm{Mg} \mathrm{m}^{-3}, \quad \lambda($ Мо $K \alpha)=0.71069 \AA$, $\mu($ Mo $K \alpha)=7.894 \mathrm{~mm}^{-1}, \quad F(000)=520, \quad$ 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 $\mathrm{Pt}-\mathrm{Cl}$ bond distances are 2.292 (3) $\AA$. The $\mathrm{Pt}-\mathrm{S}$ bond lengths [ 2.292 (2) $\AA$ ] are significantly longer than the corresponding distances in the cis isomer. The packing consists of layers of molecules parallel to the $a b$ plane.

Introduction. When $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ reacts with sulfoxide ligands $(L)$ in water, trans $-\left[\mathrm{Pt}(L)_{2} \mathrm{Cl}_{2}\right]$ 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 $\mathrm{Pt}^{11}$ disubstituted complexes except with a very sterically demanding ligand, diisoamyl sulfoxide, which gave only the trans isomer (Price et al., 1972). With $\mathrm{Me}_{2} \mathrm{SO}$ 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 $v(\mathrm{Pt}-\mathrm{Cl})$. For example cis-[ $\mathrm{Pt}(\mathrm{bmso})_{2}-$ $\mathrm{Cl}_{2}$ ] absorbs at 331 and $311 \mathrm{~cm}^{-1}$ while the trans isomer shows only one band at $349 \mathrm{~cm}^{-1}$. The colors of the two isomers are also quite different. The cis © 1988 International Union of Crystallography


[^0]:    * 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 CHI 2HU, England.

