Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Pt–Cl(1)	2·301 (1)	Cl(1)–Pt–Cl(2)	176·97 (4)
Pt–Cl(2)	2·305 (1)	Cl(1)–Pt–P(1)	92·63 (4)
Pt–P(1)	2·327 (1)	Cl(1)–Pt–P(2)	86·23 (4)
Pt–P(2)	2·316 (1)	Cl(2)–Pt–P(1)	90·00 (4)
		Cl(2)–Pt–P(2)	91·09 (4)
P(1)–C(1)	1·841 (3)	P(1)–Pt–P(2)	177·62 (4)
P(1)–C(7)	1·854 (4)		
P(1)–C(13)	1·845 (4)	Pt–P(1)–C(1)	111·4 (1)
		Pt–P(1)–C(7)	113·4 (1)
P(2)–C(19)	1·822 (4)	Pt–P(1)–C(13)	112·2 (1)
P(2)–C(25)	1·821 (3)	C(1)–P(1)–C(7)	111·1 (2)
P(2)–C(31)	1·817 (4)	C(1)–P(1)–C(13)	104·9 (2)
		C(7)–P(1)–C(13)	103·2 (2)
		Pt–P(2)–C(19)	107·9 (1)
		Pt–P(2)–C(25)	117·6 (1)
		Pt–P(2)–C(31)	116·3 (1)
		C(19)–P(2)–C(25)	107·0 (2)
		C(19)–P(2)–C(31)	105·9 (2)
		C(25)–P(2)–C(31)	101·1 (2)

		Distances		Angles	
Ring		Mean	Range	Mean	Range
A	C(1)–C(6)	1·527 (9)	1·513–1·537	110·6 (10)	109·3–111·8
B	C(7)–C(12)	1·525 (6)	1·514–1·535	110·8 (8)	109·8–111·7
C	C(13)–C(18)	1·525 (8)	1·512–1·538	111·0 (5)	110·3–111·8
D	C(19)–C(24)	1·379 (14)	1·356–1·394	120·0 (5)	118·9–120·3
E	C(25)–C(30)	1·378 (13)	1·350–1·389	120·0 (5)	119·2–120·6
F	C(31)–C(36)	1·378 (9)	1·363–1·389	120·0 (9)	118·1–121·1

References

ALYEA, E. C., DIAS, S. A., FERGUSON, G. & RESTIVO, R. J. (1977). *Inorg. Chem.* **16**, 2329–2334.

Bond Index of the Determination of Inorganic Crystal Structures (1969–1981). Institute for Materials Research, Hamilton, Canada.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Enraf–Nonius (1982). *VAX Structure Determination Package.* Enraf–Nonius, Delft.

FERGUSON, G., ROBERTS, P. J., ALYEA, E. C. & KHAN, M. (1978). *Inorg. Chem.* **17**, 2965–2967.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P. (1982). Editor. *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

RICHARDSON, J. & PAYNE, N. (1977). *Can. J. Chem.* **55**, 3203–3210.

SMITH, J. D. & OLIVER, J. D. (1978). *Inorg. Chem.* **17**, 2585–2589.

TOLMAN, C. A. (1970). *J. Am. Chem. Soc.* **92**, 2956–2965.

TOLMAN, C. A. (1977). *Chem. Rev.* **77**, 313–348.

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Structure of a Cyclization Product of a Cobalt-Mediated Hetero [2 + 2 + 2] Cycloaddition

BY J. T. RIGSBEE

Department of Chemistry, University of California, Berkeley, CA 94720, *USA*

D. KNELLER

Department of Biophysics, University of California, Berkeley, CA 94720, *USA*

AND T. M. GARRETT*

Department of Chemistry, University of California, Berkeley, CA 94720, *USA*

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Abstract. (η^5-Cyclopentadienyl)(1,2,3,11b-η^4-3-methoxy-7-oxo-2-trimethylsilyl-3a-*endo*,4,5,6,7,11c-*endo*-hexahydro-1*H*-pyrrolo[3,2,1-*de*]phenanthridine)cobalt, $[Co(C_5H_5)(C_{19}H_{23}NO_2Si)]$, $M_r = 449{\cdot}6$, monoclinic, $P2_1/n$, $a = 15{\cdot}891$ (2), $b = 8{\cdot}825$ (1), $c = 15{\cdot}185$ (2) Å, $\beta = 96{\cdot}45$ (1)°, $V = 2116{\cdot}1$ (4) Å^3, $Z = 4$, $D_m = 1{\cdot}38$, $D_x = 1{\cdot}41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 8{\cdot}83$ cm^{-1}, $F(000) = 944$, $T = 298$ K. The structure was refined to a final $R = 0{\cdot}025$ for 2319 unique observed reflections. The product heterocycle and the cyclopentadienyl ligand form a distorted sandwich about the cobalt atom. The dihedral angle between the planes of the sandwich fragments is 9·2°. The cobalt-to-cyclopentadienyl-centroid distance is 1·686 Å, and the average distance from the cobalt to the carbons of the heterocyclic diene is 2·021 Å.

Introduction. The title compound (2) was one of two products (both shown in the scheme) of a cobalt-mediated hetero [2 + 2 + 2] cycloaddition reaction. The regiochemistry of this hetero reaction, although similar to the non-hetero systems studied extensively by Vollhardt and his group (Vollhardt, 1984), is not well understood. The relative positions of the trimethylsilyl

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* To whom correspondence should be addressed.

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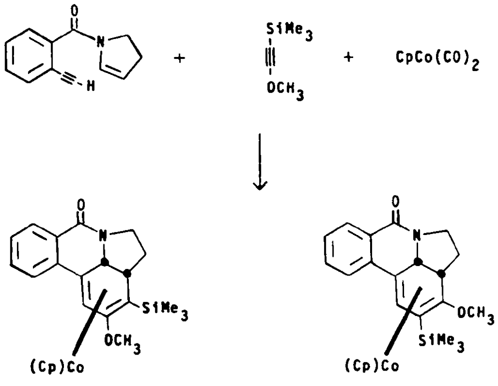
and methoxy groups were tentatively assigned on the basis of NMR spectroscopic data (Grotjahn, 1985), but were not proven until this structure was determined.



Hetero [2 + 2 + 2] cycloaddition scheme for the synthesis of the title compound.

Experimental. Pentagonal red crystals, D_m by flotation in $CH_2Cl_2/CHCl_3$. Sample crystal 0·22 × 0·16 × 0·27 mm. Laue symmetry from photographs and systematic absences $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$ consistent with the space group $P2_1/n$. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$, graphite monochromator; ω–2θ scan mode, 2θ from 3 to 45°, 2θ speed variable: 1·4–13·4° min^{-1}; h $-18\rightarrow0$, k $0\rightarrow10$, l $-17\rightarrow17$; less than 2% increase or decrease in intensity in three intensity standards and less than 1% change in three orientation standards during data collection. 3106 reflections collected, 2762 unique, 2319 having $F_o^2 > 3\sigma(F_o^2)$; data converted to structure factor amplitudes and their e.s.d.'s by correction for scan speed, background, and Lorentz and polarization effects (*SDP*: Frenz, 1982). Numerical absorption correction ($T_{\min} = 0{\cdot}74$, $T_{\max} = 0{\cdot}88$). Cobalt atom found by Patterson method, remaining non-H atoms by Fourier synthesis; anisotropic temperature factors; H atoms located in difference Fourier map, placed at calculated positions but not refined; secondary-extinction coefficient = 9·9 (2·9) × 10^{-8} (Zachariasen, 1963). Least squares, $\sum w(\Delta F)^2$ minimized, $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (pF^2)^2$, $p = 0{\cdot}03$. Final least-squares cycle $R = 0{\cdot}025$, $wR = 0{\cdot}035$, $S = 1{\cdot}66$, $(\Delta/\sigma)_{\max} < 0{\cdot}01$. Highest peak in final difference

Table 1. *Positional parameters (e.s.d.'s in parentheses)*

$B_{eq} = \frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

The general temperature factor expression is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

	x	y	z	B_{eq}(Å^2)
Co	0·23383 (2)	0·09363 (3)	0·07983 (2)	2·341 (6)
Si	0·36266 (4)	0·35886 (8)	−0·00170 (4)	2·77 (1)
O(1)	−0·0942 (1)	0·3786 (2)	−0·0872 (1)	4·92 (5)
O(2)	0·3046 (1)	0·0699 (2)	−0·0977 (1)	3·43 (4)
N	0·0199 (1)	0·2260 (2)	−0·0885 (1)	3·31 (5)
C(1)	0·2448 (2)	−0·1318 (3)	0·1096 (2)	3·68 (6)
C(2)	0·2039 (2)	−0·0573 (3)	0·1737 (2)	3·82 (6)
C(3)	0·2599 (2)	0·0518 (3)	0·2164 (2)	3·98 (6)
C(4)	0·3348 (2)	0·0459 (3)	0·1774 (2)	3·93 (6)
C(5)	0·3257 (2)	−0·0652 (3)	0·1103 (2)	3·80 (6)
C(6)	0·1209 (1)	0·2049 (3)	0·0444 (1)	2·36 (5)
C(7)	0·1934 (1)	0·3003 (3)	0·0486 (1)	2·37 (5)
C(8)	0·2595 (1)	0·2567 (3)	−0·0029 (1)	2·32 (5)
C(9)	0·2373 (1)	0·1238 (3)	−0·0544 (2)	2·45 (5)
C(10)	0·1504 (2)	0·1064 (3)	−0·1046 (2)	2·72 (5)
C(11)	0·1281 (2)	0·2224 (3)	−0·1794 (2)	3·64 (6)
C(12)	0·0330 (2)	0·2432 (3)	−0·1813 (2)	4·10 (6)
C(13)	0·0849 (1)	0·1304 (3)	−0·0403 (2)	2·57 (5)
C(14)	−0·0376 (2)	0·3022 (3)	−0·0474 (2)	3·47 (6)
C(15)	−0·0270 (1)	0·2896 (3)	0·0516 (2)	3·10 (5)
C(16)	−0·0931 (2)	0·3343 (3)	0·0980 (2)	4·25 (6)
C(17)	−0·0848 (2)	0·3335 (3)	0·1886 (2)	4·77 (7)
C(18)	−0·0086 (2)	0·2934 (4)	0·2347 (2)	4·70 (7)
C(19)	0·0593 (2)	0·2515 (3)	0·1898 (2)	3·80 (6)
C(20)	0·0510 (1)	0·2460 (3)	0·0982 (2)	2·84 (5)
C(21)	0·3005 (2)	−0·0830 (3)	−0·1261 (2)	4·86 (7)
C(22)	0·3581 (2)	0·4627 (4)	−0·1087 (2)	4·57 (7)
C(23)	0·4571 (2)	0·2328 (3)	0·0106 (2)	4·34 (7)
C(24)	0·3716 (2)	0·4942 (3)	0·0925 (2)	4·44 (7)

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

Co–C(1)	2·044 (2)	C(15)–C(20)	1·410 (3)
Co–C(2)	2·045 (2)	C(16)–C(17)	1·368 (3)
Co–C(3)	2·101 (2)	C(17)–C(18)	1·375 (3)
Co–C(4)	2·100 (2)	C(18)–C(19)	1·389 (3)
Co–C(5)	2·039 (2)	C(19)–C(20)	1·383 (3)
Co–Cp	1·686	N–C(12)	1·457 (3)
Co–C(6)	2·064 (2)	N–C(13)	1·464 (2)
Co–C(7)	1·974 (2)	N–C(14)	1·343 (3)
Co–C(8)	1·982 (2)	O(1)–C(14)	1·227 (2)
Co–C(9)	2·062 (2)	O(2)–C(9)	1·399 (2)
C(6)–C(7)	1·422 (2)	O(2)–C(21)	1·417 (3)
C(6)–C(13)	1·500 (3)	Si–C(8)	1·870 (2)
C(6)–C(20)	1·496 (3)	Si–C(22)	1·860 (2)
C(7)–C(8)	1·431 (2)	Si–C(23)	1·860 (2)
C(8)–C(9)	1·431 (2)	Si–C(24)	1·856 (2)
C(9)–C(10)	1·508 (3)	Cyclopentadienyl	C–C
C(10)–C(11)	1·541 (3)	Range	1·389 (3)
C(10)–C(13)	1·519 (3)		1·417 (3);
C(11)–C(12)	1·519 (3)	Average	1·404
C(14)–C(15)	1·498 (3)		
C(15)–C(16)	1·386 (3)		
C(7)–C(6)–C(13)	121·78 (15)	C(14)–C(15)–C(16)	118·84 (19)
C(7)–C(6)–C(20)	118·66 (16)	C(14)–C(15)–C(20)	121·17 (17)
C(13)–C(6)–C(20)	109·89 (15)	C(16)–C(15)–C(20)	119·75 (20)
C(6)–C(7)–C(8)	117·19 (16)	C(15)–C(16)–C(17)	121·13 (21)
C(7)–C(8)–C(9)	111·62 (15)	C(16)–C(17)–C(18)	119·54 (21)
C(7)–C(8)–Si	124·17 (13)	C(17)–C(18)–C(19)	120·44 (22)
C(9)–C(8)–Si	124·21 (13)	C(18)–C(19)–C(20)	120·77 (20)
C(8)–C(9)–C(10)	120·99 (16)	C(6)–C(20)–C(15)	117·16 (17)
C(8)–C(9)–O(2)	112·40 (15)	C(6)–C(20)–C(19)	124·45 (17)
C(10)–C(9)–O(2)	115·61 (15)	C(15)–C(20)–C(19)	118·30 (17)
C(9)–C(10)–C(11)	115·22 (16)	C(12)–N–C(13)	111·94 (16)
C(9)–C(10)–C(13)	108·42 (15)	C(12)–N–C(14)	125·16 (17)
C(13)–C(10)–C(11)	105·26 (16)	C(13)–N–C(14)	122·39 (17)
C(10)–C(11)–C(12)	103·90 (16)	C(9)–O(2)–C(21)	117·11 (16)
C(11)–C(12)–N	102·66 (15)	C(8)–Si–C(22)	106·31 (9)
N–C(13)–C(6)	110·81 (15)	C(8)–Si–C(23)	114·16 (9)
N–C(13)–C(10)	104·84 (15)	C(8)–Si–C(24)	108·01 (9)
C(6)–C(13)–C(10)	112·91 (15)	C(22)–Si–C(23)	109·56 (10)
O(1)–C(14)–N	123·06 (21)	C(22)–Si–C(24)	110·35 (11)
O(1)–C(14)–C(15)	121·91 (20)	C(23)–Si–C(24)	108·42 (11)
N–C(14)–C(15)	115·01 (18)		
C(13)–C(6)–C(7)–C(8)	−38·1	C(19)–C(20)–C(6)–C(7)	−63·6
C(6)–C(7)–C(8)–C(9)	3·0	C(6)–Co–Cp–C(2)	14·6
C(7)–C(8)–C(9)–C(10)	44·0	C(7)–Co–Cp–C(3)	12·1
Si–C(8)–C(9)–O(2)	5·6	C(8)–Co–Cp–C(4)	26·0
C(16)–C(15)–C(14)–O(1)	15·6	C(9)–Co–Cp–C(5)	20·9

Fourier map = 0·217 e Å^{-3}. Atomic scattering factors of all atoms and f' and f'' values for non-hydrogen atoms taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 gives the final atomic positional parameters, and Table 2 lists the main bond lengths, bond angles and torsion angles.* A view of the title compound is shown in Fig. 1, which explains the atom-numbering scheme.

The sandwich fragments about the cobalt are nearly parallel with a dihedral angle between the plane of the diene carbons and the plane of the cyclopentadienyl of 9·2°. The diene carbons are neither staggered nor eclipsed with respect to the Cp carbons; the torsion angles vary from 12·1 to 26·0°. The hydrogens on C(10) and C(13) are found to be *syn* to the cobalt and *cis* to each other. All other bond lengths and angles are within normal values.

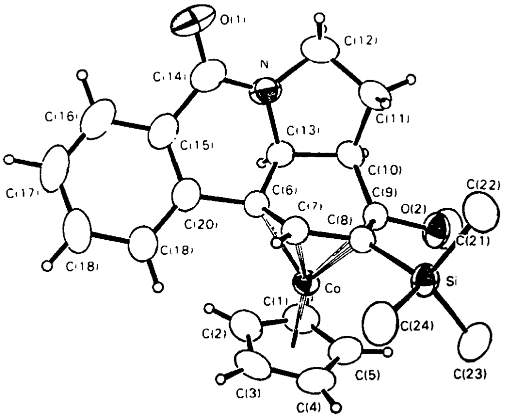


Fig. 1. Molecular structure with crystallographic numbering scheme. The ellipsoids are scaled to represent the 60% probability surface. Hydrogen atoms are given arbitrarily small spheres for clarity.

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References

FRENZ, B. A. (1982). *Structure Determination Package*. College Station, Texas, and Enraf–Nonius, Delft; as revised locally by Dr F. J. HOLLANDER.

GROTJAHN, D. (1985). Personal communication.

International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

VOLLHARDT, K. P. C. (1984). *Angew. Chem. Int. Ed. Engl.* **23**(8), 539–556.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **18**, 1139–1144.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes calculations, intramolecular distances and angles, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43126 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of an Acetonitrile Complex of Platinum(II): Tetraethylammonium Acetonitriletribromoplatinate(II)

BY MARIEL M. MUIR, GRISELL M. GOMEZ AND JAMES A. MUIR

Departments of Chemistry and Physics, University of Puerto Rico, Rio Piedras, PR 00931, *USA*

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Abstract. $[N(C_2H_5)_4][PtBr_3(CH_3CN)]$, $M_r = 606·1$, triclinic, $P\bar{1}$, $a = 8·890$ (1), $b = 13·042$ (3), $c = 7·695$ (1) Å, $\alpha = 96·17$ (1), $\beta = 98·25$ (1), $\gamma = 103·62$ (2)°, $V = 848·81$ Å^3, $Z = 2$, $D_x = 2·37$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 148·59$ cm^{-1}, $F(000) = 560$, $T = 296$ K, final $R = 0·040$ for 2212 observed reflections. The $[PtBr_3(CH_3CN)]^-$ unit has square-planar geometry about the Pt, with the acetonitrile coordinated to the Pt in a nearly linear manner through the N. The Br *trans* to the N is about 0·04 Å closer to the Pt than the other two Br atoms, which clearly shows the lower *trans* influence of acetonitrile compared to Br.

Introduction. Platinum(II) amine complexes have been widely studied since the discovery in 1965 of the biological activity of *cis*-diamminedichloroplatinum(II) (Rosenberg, Van Camp & Krigas, 1965). The reaction of halogen-bridged complexes of platinum(II) and

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