

nically in the series of squaric-acid derivatives so far characterized structurally, *i.e.* $C_4O_4^{2-}$ (Macintyre & Werkema, 1964), $C_4S_4^{2-}$ (Allmann *et al.*, 1976), 1,2-DTSA and 1,3-DTSA (Mattes *et al.*, 1982), where mean C—C distances from 1.438 (7) to 1.461 (4) Å have been found. The C—S bond length [1.672 (2) Å] is slightly longer than in 1,2-DTSA and 1,3-DTSA, where the values 1.645 (3) and 1.652 (7) Å have been found and no hydrogen bonds can be formed. In the present case, the S atom is engaged in a hydrogen bond [S...O(2): 3.352 (1) Å, S—H(1)...O(2): 167 (2)°]. The same is valid in $C_4S_4^{2-}$ with the C—S bond length 1.663 (8) Å.

The C—O bond length [1.236 (2) Å] agrees well with the estimated bond order 1.5. Potassium is seven-coordinated by two S atoms at distances 3.469 (1) and 3.445 (1) Å and five O atoms [mean distance 2.795 (1) Å]. In the three-dimensional lattice, the

planes of the dianions are aligned nearly parallel to the *a* axis, with an approximate angle of 45° between neighboring anions (see Fig. 2).

References

- ALLMANN, R., DEBAERDEMAEKER, T., MANN, K., MATUSCH, R., SCHMIEDEL, R. & SEITZ, G. (1976). *Chem. Ber.* **109**, 2208–2215.
 FATIADI, A. J. (1980). *J. Org. Chem.* **45**, 1338–1339.
 MACINTYRE, W. M. & WERKEMA, M. S. (1964). *J. Chem. Phys.* **40**, 3563–3568.
 MATTES, R., ALTMIEPPEN, D., JOHANN, G., SCHULTE-COERNE, M. & WEBER, H. (1982). *Monatsh. Chem.* **113**, 191–196.
 SCHMIDT, A. H. (1980). *Synthesis*, pp. 961–994, and literature cited therein.
 SEITZ, G. (1980). *Nachr. Chem. Tech.* **28**, 804–807, and literature cited therein.
 SEITZ, G., MANN, R., SCHMIEDEL, R. & MATUSCH, R. (1979). *Chem. Ber.* **112**, 990–999.
 Syntax (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California.

Acta Cryst. (1984). **C40**, 742–746

Structures of Azidobis(dimethylglyoximato)(triphenylphosphine)cobalt(III), $C_{26}H_{29}CoN_7O_4P$, and [4,5-Bis(methoxycarbonyl)-1,2,3-triazolato]-bis(dimethylglyoximato)(triphenylphosphine)cobalt(III), $C_{32}H_{35}CoN_7O_8P^*$

By J. H. NELSON AND N. E. TAKACH

Department of Chemistry, University of Nevada, Reno, Nevada 89557, USA

AND N. BRESCIANI-PAHOR, L. RANDACCIO AND E. ZANGRANDO

Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy

(Received 3 November 1983; accepted 5 December 1983)

Abstract. $(PPh_3)Co(DH)_2N_3$, $M_r = 593.5$, orthorhombic, $Pca2_1$, $a = 15.156$ (8), $b = 11.120$ (6), $c = 16.557$ (8) Å, $U = 2790$ (3) Å³, $Z = 4$, $D_m = 1.42$ (floatation), $D_x = 1.41$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.7107$ Å, $\mu = 7.5$ cm⁻¹, $F(000) = 1232$, $T = 298$ K, $R = 0.025$ for 1988 independent reflections. $(PPh_3)Co(DH)_2(trz)$, $M_r = 735.6$, triclinic, $P\bar{1}$, $a = 10.261$ (6), $b = 18.190$ (9), $c = 10.425$ (6) Å, $\alpha = 76.01$ (6), $\beta = 88.15$ (6), $\gamma = 110.19$ (6)°, $U = 1758$ (2) Å³, $Z = 2$, $D_m = 1.41$ (floatation), $D_x = 1.39$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.7107$ Å, $\mu = 6.2$ cm⁻¹, $F(000) = 764$, $T = 298$ K, $R = 0.037$ for 4469 independent reflections. The cobalt atom is octahedrally distorted with the $(DH)_2$ (DH = monoanion of dimethylglyoxime) units at the equatorial positions in both compounds. The N—Co—P fragment is characterized by Co—P, Co—N bond lengths of 2.311 (1) and 2.014 (4) Å, respectively, and an N—Co—P angle of 175.4 (1)° in the azido

derivative(I). The corresponding figures for the triazolato (trz) derivative (II) are 2.333 (1), 1.953 (3) Å and 178.0 (1)°, respectively. The *trans* influence of the axial ligands is discussed and compared with that of other ligands.

Introduction. The reaction products of substituted alkynes with $LCo(DH)_2N_3$ complexes (L = neutral ligand) have been characterized by elemental analyses. IR and ¹H NMR spectroscopy (Beck, Nelson, Takach, Kemmerich, Boehme & Jablonski, 1982). These data suggest that a 1,3-dipolar cycloaddition takes place, yielding complexes in which the substituted triazolato is coordinated to cobalt. Spectroscopic data suggested that the coordination takes place through the central N atom of the triazolato ring. Furthermore, it was suggested that the triazolato group has a greater *trans* labilizing ability than azide does. Since the determination of the molecular geometry may give an

* Dimethylglyoxime is 2,3-butanedione dioxime.

indication about the above points we have undertaken the X-ray analysis of the title compounds, hereinafter called (I) and (II), respectively.

Experimental. Crystals of (I) and (II) obtained as described by Beck *et al.*; for (I) and (II), cell parameters determined by Weissenberg and precession photographs, crystal $0.6 \times 0.4 \times 0.7$ (I) and $0.4 \times 0.5 \times 0.6$ (II) mm, and refined on a Siemens AED single-crystal diffractometer using 20 carefully centred high-angle ($15 < \theta < 20^\circ$) reflections; θ - 2θ scan, 2θ range 6 - 56° ; one standard reflection [319 (I) and 751 (II)] every 100 measured showed no decay ($<2\%$); 3784 (I) (h 0-20, k 0-15, l 0-22) and 8899 (II) (h -13-13, k -22-22, l 0-13) data measured, 1988 (I) and 4469 (II) with $I > 3\sigma(I)$ used in the following calculations, Lorentz and polarization but no absorption corrections; both (I) and (II) solved by conventional Patterson and Fourier methods and refined on F by block-diagonal anisotropic least squares to final R 0.025 (I) and 0.037 (II) and R_w 0.032 (I) and 0.052 (II); contribution of hydrogen atoms at calculated positions [MeO hydrogens of (II) were not included] was held constant ($B = 5 \text{ \AA}^2$) in both structures; in the final refinement, $w = 1/(A + |F_o| + B|F_c|^2)$ where $A = 20.6$ (I) and 10.8 (II) and $B = 0.009$ (I) and 0.017 (II) were chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $(\sin\theta/\lambda)$. 352 (I) and 443 (II) refined parameters, max. $\Delta/\sigma = 0.8$ (I) and 0.2 (II); $|\Delta\rho|$ on final map 0.6 e \AA^{-3} for (I) and (II); space group $Pca2_1$ choice for (I) was based on statistical test and structure refinement;* atomic scattering factors from Moore (1963); all calculations performed with XRAY70 (Stewart, Kundell & Baldwin, 1970).

Discussion. Final non-hydrogen positional parameters are collected in Table 1. Fig. 1 shows a perspective view of the crystallographically independent molecule of (I) with the numbering scheme for the atoms. The coordination about the cobalt atom is roughly octahedral. Two dimethylglyoxime monoanions (DH) occupy the equatorial positions, the triphenylphosphine and azide groups occupying the axial positions. Bond lengths and angles of interest are given in Table 2.

The cobalt atom is displaced 0.081 (3) \AA from the plane of the four equatorial N donors [coplanar within ± 0.009 (5) \AA] towards PPh_3 . The two DH units are bent towards the N_3 group, their planes making a dihedral angle of 5.7 (1) $^\circ$. Bond lengths and angles in

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39092 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the $\text{Co}(\text{DH})_2\text{PPh}_3$ moiety fall within the range found for similar compounds (Bresciani-Pahor, Calligaris & Randaccio, 1980, and references cited therein). The $\text{Ph}_3\text{P}-\text{Co}-\text{N}_3$ fragment is characterized by a $\text{P}-\text{Co}-\text{N}$ angle of 175.4 (1) $^\circ$ and $\text{Co}-\text{P}$ and $\text{Co}-\text{N}(5)$ bond lengths of 2.311 (1) and 2.014 (4) \AA , respectively. The $\text{Co}-\text{N}(5)-\text{N}(6)$ and $\text{N}(5)-\text{N}(6)-\text{N}(7)$ bond angles are 120.4 (3) and 177.6 (6) $^\circ$, respectively. The $\text{N}(5)-\text{N}(6)$ and $\text{N}(6)-\text{N}(7)$ distances are 1.180 (6) and 1.161 (7) \AA , respectively. The latter distances differ only within three times their e.s.d.'s.

The azide group lies above the DH unit which includes $\text{N}(1)$ and $\text{N}(2)$ atoms, but, as a whole, it is slightly shifted to the opposite side. In fact, the $\text{N}(5)-\text{Co}-\text{N}(1)$ and $\text{N}(5)-\text{Co}-\text{N}(2)$ angles of 89.1 (2) and 88.7 (2) $^\circ$, respectively, are larger than the $\text{N}(5)-\text{Co}-\text{N}(3)$ and $\text{N}(5)-\text{Co}-\text{N}(4)$ angles of 85.5 (2) and 86.8 (2) $^\circ$.

Fig. 2 shows the view along the $\text{Co}-\text{P}$ direction of (II), with the numbering scheme for the triazolate atoms. The DH units occupy the equatorial positions whereas PPh_3 and the triazolate ion on the axial ones. The triazolate ion is bonded to cobalt through its central $\text{N}(5)$ atom.

The cobalt atom is displaced by 0.041 (3) \AA from the plane of the four N equatorial donors [coplanar within ± 0.001 (4) \AA] towards PPh_3 . The two DH units are bent towards the triazolate group, their planes making a dihedral angle of 4.2 (2) $^\circ$. Bond lengths and angles in the $\text{Co}(\text{DH})_2\text{PPh}_3$ moiety fall within the range found for similar compounds (Bresciani-Pahor, Calligaris & Randaccio, 1980, and references cited therein). The $\text{P}-\text{Co}-\text{N}(5)$ fragment is characterized by a $\text{P}-\text{Co}-\text{N}$ angle of 178.0 (1) $^\circ$ and $\text{Co}-\text{P}$ and $\text{Co}-\text{N}$ distances of 2.333 (1) and 1.953 (3) \AA , respectively.

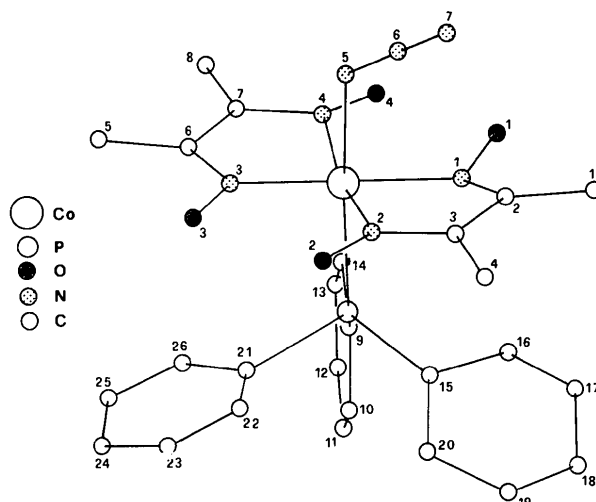


Fig. 1. A perspective view of the molecule of (I) together with the numbering scheme of the atoms.

Table 1. Positional parameters ($\times 10^4$) of non-hydrogen atoms of (I) and (II)

Compound (I)	E.s.d.'s are given in parentheses.			$B_{eq}(\text{\AA}^2)^*$
	x	y	z	
Co	4655.0 (3)	2457.4 (4)	2500	1.92 (1)
P	4564 (1)	3308 (1)	1229 (1)	2.01 (3)
O(1)	6311 (2)	3559 (3)	2888 (2)	3.5 (1)
O(2)	4336 (2)	190 (2)	1758 (2)	3.3 (1)
O(3)	3012 (2)	1278 (3)	2269 (2)	3.6 (1)
O(4)	4988 (2)	4642 (3)	3366 (2)	3.3 (1)
N(1)	5896 (2)	2605 (3)	2559 (3)	2.5 (1)
N(2)	4945 (2)	995 (3)	2007 (2)	2.5 (1)
N(3)	3409 (2)	2265 (3)	2547 (3)	2.8 (1)
N(4)	4363 (2)	3883 (3)	3082 (2)	2.7 (1)
N(5)	4669 (3)	1610 (3)	3575 (2)	3.4 (2)
N(6)	5248 (3)	947 (4)	3741 (3)	3.9 (2)
N(7)	5814 (4)	303 (6)	3933 (4)	8.3 (3)
C(1)	7342 (3)	1604 (4)	2321 (3)	4.3 (2)
C(2)	6348 (3)	1696 (4)	2280 (2)	2.8 (2)
C(3)	5795 (3)	750 (3)	1942 (3)	2.6 (1)
C(4)	6134 (4)	-359 (5)	1544 (4)	5.1 (2)
C(5)	1977 (3)	3061 (6)	3009 (4)	5.2 (2)
C(6)	2968 (3)	3118 (4)	2908 (3)	3.3 (2)
C(7)	3533 (3)	4075 (4)	3218 (3)	3.3 (2)
C(8)	3195 (4)	5162 (5)	3651 (3)	4.6 (2)
C(9)	4563 (2)	4941 (3)	1072 (2)	2.3 (1)
C(10)	4532 (3)	5336 (3)	268 (3)	2.9 (2)
C(11)	4486 (3)	6562 (4)	93 (3)	3.4 (2)
C(12)	4470 (3)	7399 (4)	712 (3)	3.3 (2)
C(13)	4511 (3)	7017 (4)	1503 (3)	3.7 (2)
C(14)	4562 (3)	5786 (4)	1686 (3)	3.4 (2)
C(15)	5497 (3)	2869 (4)	587 (3)	2.7 (1)
C(16)	6319 (3)	3341 (4)	803 (3)	3.3 (2)
C(17)	7089 (3)	3021 (5)	390 (3)	4.1 (2)
C(18)	7043 (3)	2209 (5)	-231 (4)	4.8 (2)
C(19)	6234 (4)	1767 (5)	-477 (4)	5.2 (3)
C(20)	5458 (3)	2079 (5)	-73 (3)	4.2 (2)
C(21)	3527 (2)	2864 (4)	740 (2)	2.4 (1)
C(22)	3402 (3)	1745 (4)	384 (3)	3.3 (2)
C(23)	2591 (4)	1467 (4)	17 (4)	4.2 (2)
C(24)	1902 (3)	2267 (5)	54 (3)	4.3 (2)
C(25)	1995 (3)	3351 (5)	453 (3)	4.0 (2)
C(26)	2812 (3)	3656 (4)	796 (3)	3.1 (2)
Compound (II)				
Co	-81.5 (4)	2512.7 (2)	290.0 (4)	1.95(1)
P	-1535 (1)	2650.0 (5)	-1355 (1)	2.32(2)
O(1)	584 (3)	4187 (1)	133 (3)	3.5 (1)
O(2)	-2248 (2)	1138 (1)	1987 (2)	3.3 (1)
O(3)	-599 (3)	828 (1)	567 (3)	3.9 (1)
O(4)	2193 (2)	3882 (1)	-1311 (2)	3.4 (1)
O(5)	4148 (3)	4037 (2)	3007 (3)	4.5 (1)
O(6)	4663 (3)	2994 (2)	4170 (4)	5.5 (2)
O(7)	1901 (6)	574 (2)	4056 (5)	9.3 (3)
O(8)	2541 (6)	1354 (3)	5434 (4)	9.3 (3)
N(1)	-268 (3)	3417 (1)	750 (3)	2.6 (1)
N(2)	-1655 (3)	1947 (1)	1619 (2)	2.6 (1)
N(3)	167 (3)	1607 (1)	-119 (3)	2.9 (1)
N(4)	1548 (3)	3073 (1)	-988 (3)	2.5 (1)
N(5)	1133 (3)	2432 (1)	1680 (2)	2.5 (1)
N(6)	2131 (3)	3069 (2)	1914 (3)	2.6 (1)
N(7)	1063 (3)	1720 (2)	2464 (3)	3.4 (1)
C(1)	-1568 (5)	3909 (3)	2163 (4)	4.3 (2)
C(2)	-1257 (4)	3261 (2)	1695 (3)	2.8 (1)
C(3)	-2057 (3)	2390 (2)	2237 (3)	2.8 (1)
C(4)	-3201 (5)	2034 (3)	3381 (4)	4.7 (2)
C(5)	1630 (6)	1105 (3)	-1329 (6)	6.3 (2)
C(6)	1218 (4)	1755 (2)	-1000 (4)	3.5 (1)
C(7)	2005 (4)	2633 (2)	-1555 (3)	3.1 (1)
C(8)	3203 (4)	2974 (3)	-2653 (4)	4.4 (2)
C(9)	-511 (3)	3207 (2)	-3005 (3)	2.8 (1)
C(10)	-446 (4)	2758 (3)	-3908 (4)	3.9 (2)
C(11)	354 (5)	3146 (3)	-5157 (4)	5.0 (2)
C(12)	1098 (5)	3954 (3)	-5488 (4)	5.5 (2)
C(13)	1072 (4)	4414 (3)	-4591 (4)	5.0 (2)
C(14)	278 (4)	4034 (2)	-3339 (4)	3.7 (2)
C(15)	-2824 (4)	1771 (2)	-1747 (3)	3.5 (1)
C(16)	-3729 (4)	1938 (3)	-2655 (4)	4.5 (2)
C(17)	-4715 (5)	1314 (4)	-3035 (5)	5.9 (2)
C(18)	-4820 (6)	535 (4)	-2515 (6)	8.0 (3)
C(19)	-3941 (9)	365 (4)	-1638 (8)	11.2 (5)
C(20)	-2929 (7)	989 (3)	-1243 (6)	7.6 (3)
C(21)	-2692 (3)	3161 (2)	-938 (3)	3.8 (1)
C(22)	-2389 (4)	3993 (2)	-1320 (4)	3.8 (2)
C(23)	-3340 (5)	4321 (3)	-925 (4)	4.6 (2)

Table 1 (cont.)

	x	y	z	$B_{eq}(\text{\AA}^2)^*$
C(24)	-4587 (4)	3813 (3)	-142 (4)	4.5 (2)
C(25)	-4891 (4)	2983 (3)	264 (4)	4.4 (2)
C(26)	-3952 (4)	2651 (2)	-121 (4)	3.6 (2)
C(27)	2735 (3)	2748 (2)	2933 (3)	2.6 (1)
C(28)	3939 (3)	3254 (2)	3440 (3)	3.1 (1)
C(29)	5345 (5)	4596 (3)	3428 (6)	6.1 (2)
C(30)	2065 (4)	1906 (2)	3265 (3)	3.2 (1)
C(31)	2240 (5)	1257 (3)	4323 (4)	5.1 (2)
C(32)	1916 (9)	-133 (4)	5133 (8)	11.1 (5)

$$* B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Relevant bond lengths (\AA) and bond angles ($^\circ$) for (I) and (II)

	(I)	(II)	(I)	(II)
Co—P	2.311 (1)	2.333 (1)	P—Co—N(5)	175.4 (1) 178.0 (1)
Co—N(5)	2.014 (4)	1.953 (3)	N(1)—Co—P	94.1 (1) 89.08 (9)
Co—N(1)	1.891 (3)	1.889 (3)	N(1)—Co—N(5)	89.1 (2) 88.9 (1)
Co—N(2)	1.871 (3)	1.899 (2)	N(1)—Co—N(2)	82.2 (1) 81.5 (1)
Co—N(3)	1.902 (3)	1.894 (3)	N(1)—Co—N(3)	174.5 (2) 177.4 (1)
Co—N(4)	1.908 (3)	1.906 (2)	N(1)—Co—N(4)	97.6 (2) 98.7 (1)
N(1)—O(1)	1.348 (4)	1.350 (3)	N(2)—Co—P	88.5 (1) 91.06 (8)
N(1)—C(2)	1.307 (5)	1.297 (4)	N(2)—Co—N(5)	88.7 (2) 88.8 (1)
N(2)—O(2)	1.351 (4)	1.332 (3)	N(2)—Co—N(3)	98.8 (1) 98.7 (1)
N(2)—C(3)	1.321 (5)	1.303 (5)	N(2)—Co—N(4)	175.5 (2) 177.6 (1)
N(3)—O(3)	1.333 (4)	1.356 (3)	N(3)—Co—P	91.4 (1) 93.46 (9)
N(3)—C(6)	1.305 (6)	1.301 (5)	N(3)—Co—N(5)	85.5 (2) 88.5 (1)
N(4)—O(4)	1.353 (5)	1.338 (3)	N(3)—Co—N(4)	80.9 (2) 80.9 (1)
N(4)—C(7)	1.295 (6)	1.297 (5)	N(4)—Co—P	96.1 (1) 91.37 (8)
C(1)—C(2)	1.511 (6)	1.501 (7)	N(4)—Co—N(5)	86.8 (2) 88.8 (1)
C(2)—C(3)	1.457 (6)	1.464 (4)	Co—N(5)—N(6)	120.4 (3) 124.3 (2)
C(3)—C(4)	1.490 (7)	1.494 (5)	Co—N(5)—N(7)	— 122.2 (2)
C(5)—C(6)	1.512 (7)	1.493 (8)	N(5)—N(6)—N(7)	177.6 (6) —
C(6)—C(7)	1.460 (7)	1.472 (5)	N(6)—N(5)—N(7)	— 113.6 (3)
C(7)—C(8)	1.496 (7)	1.498 (5)	N(5)—N(6)—C(27)	— 105.3 (2)
N(5)—N(6)	1.180 (6)	1.335 (3)	N(5)—N(7)—C(30)	— 105.1 (3)
N(5)—N(7)	— 1.331 (4)	—	N(6)—C(27)—C(30)	— 107.5 (3)
N(6)—N(7)	1.161 (7)	—	N(7)—C(30)—C(27)	— 108.6 (3)
N(6)—C(27)	— 1.359 (4)	—	Co—P—C(9)	122.3 (1) 111.4 (1)
N(7)—C(30)	— 1.350 (5)	—	Co—P—C(15)	111.9 (1) 122.5 (1)
C(27)—C(30)	— 1.392 (5)	—	Co—P—C(21)	110.1 (1) 110.8 (1)
P—C(9)	1.835 (4)	1.843 (3)	C(9)—P—C(15)	100.4 (2) 100.9 (2)
P—C(15)	1.836 (4)	1.833 (4)	C(9)—P—C(21)	101.7 (2) 110.3 (2)
P—C(21)	1.835 (4)	1.840 (4)	C(15)—P—C(21)	109.4 (2) 100.0 (2)

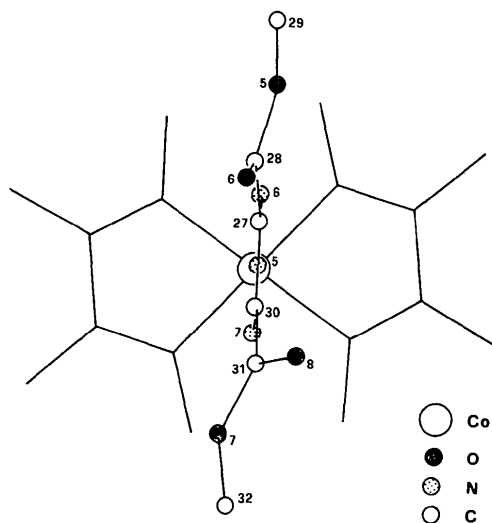
Fig. 2. A view of the molecule of (II) along the Co—P direction together with the numbering scheme of the 4,5-bis(methoxycarbonyl)-1,2,3-triazolate atoms. The numbering scheme of the Co(DH)₂PPh₃ moiety is the same as (I).

Table 3. Comparison of relevant structural parameters in $L\text{Co}(\text{DH})_2\text{N}_3$ and in $\text{PR}_3\text{Co}(\text{DH})_2\text{X}$ [$\text{X} = 5\text{-CF}_3\text{-tetrazolate; 4,5-bis(methoxycarbonyl)triazolate}$] compounds

<i>L</i>	<i>X</i>	Co– <i>L</i> (Å)	Co– <i>X</i> (Å)	<i>L</i> –Co– <i>X</i> (°)	α (°)*	<i>d</i> (Å)†
py	N_3^a	1.973 (5)	1.955 (6)	177.3 (2)	2.9 (1)	0.02
PPh_3	N_3^b	2.311 (1)	2.014 (4)	175.4 (1)	5.7 (1)	0.081 (3)
PBU_3^c	tetrazolate ^c	2.263 (2)	1.979 (6)	—	10.4 (2)	0.03
PPh_3	triazolate ^b	2.333 (1)	1.953 (3)	178.0 (1)	4.2 (2)	0.041 (3)

References: (a) Clearfield *et al.* (1978); (b) present work; (c) Takach *et al.* (1980).* Dihedral angle between the two DH units, the bending being toward *X*.† Displacement of Co from the four-N equatorial plane toward *L*.

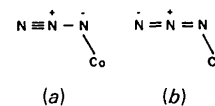
The triazolate ring atoms are coplanar within ± 0.004 (4) Å. The orientation of their plane with respect to the equatorial ligands is shown in Fig. 2. The C(28) and C(31) carbon atoms of the two side CO_2Me groups are slightly displaced above and below the triazolate plane by +0.075 (4) and –0.064 (6) Å, respectively. Furthermore, the C(28), O(5), O(6) plane makes an angle of 11.8 (3)° with the triazolate plane. The C(27) atom lies within the former plane, while the C(29) atom is slightly displaced by 0.03 (6) Å. The corresponding figures for the plane defined by the C(31), O(7), O(8) atoms are 33.2 (6)°, –0.18 (1) [C(30)] and +0.05 (1) Å [C(32)]. The planes passing through the two CO_2 groups make a dihedral angle of 39.1 (6)°. Thus, the two methoxycarbonyl groups are rotated around their C– CO_2 bonds in such a way (Fig. 2) as to put O(6) and O(8) above and below the triazolate plane, at a reciprocal distance of 2.968 (5) Å. The bond lengths and angles within the triazolate ring are given in Table 2. Their values indicate some amount of electronic delocalization over the ring which has twofold symmetry within experimental error. The mean N–N and C–N bond lengths are 1.333 (4) and 1.355 (5) Å, respectively, whereas the C–C distance is 1.392 (5) Å. The above mean values do not differ significantly from the mean values of 1.318 (10) and 1.330 (10) Å found for N–N and C–N bonds in the tetrazolate analogue (Takach, Holt, Alcock, Henry & Nelson, 1980).

It is of interest to compare the structure of (I) with the corresponding $\text{pyCo}(\text{DH})_2\text{N}_3$ (py = pyridine) compound (Clearfield, Gopal, Kline, Sipski & Urban, 1978). Some structural parameters are reported in Table 3. As already observed (Bresciani-Pahor, Randaccio, Toscano & Marzilli, 1982), substitution of py by the bulkier PPh_3 provokes an increase of distortion in the $\text{Co}(\text{DH})_2$ unit as shown by the comparison of α and *d* values. Furthermore, a significant lengthening of the Co– N_3 bond (0.061 Å) is observed. A lengthening of the Co–Cl distance has already been observed (Marzilli, Toscano, Ramsden, Randaccio & Bresciani-Pahor, 1982) in $\text{PR}_3\text{Co}(\text{DH})_2\text{Cl}$ analogues as compared with $\text{NH}_3\text{Co}(\text{DH})_2\text{Cl}$ [from 2.235 (3) to 2.261 (4) Å] and has been attributed to the electronic *trans* influencing ability of P donor ligands greater than

that of N donor ligands. However, a contribution to the observed lengthening due to the ‘steric’ *trans* influence of PPh_3 , which is greater than that of pyridine, may not be ruled out, in view of the larger deformation induced in the equatorial ligand by PPh_3 which may provoke a lengthening of the *trans* Co–N bond (Bresciani-Pahor, Randaccio, Toscano, Sandercock & Marzilli, 1982). Whatever the origin, the observed Co–N lengthening should influence the rate constants for the cycloaddition reaction of the coordinated azide group having different *trans* ligands. An additional influence on the rate constants may also derive from the different bending of the $(\text{DH})_2$.

The Co–P bond length of 2.311 (1) Å is very close to the values reported for $\text{PPh}_3\text{Co}(\text{DH})_2\text{Cl}$ [2.327 (4) Å, Brückner & Randaccio, 1974] suggesting that N_3^- is a weak *trans*-influencing ligand, probably even weaker than Cl^- .

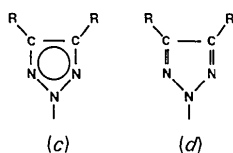
The N(5)–N(6) [1.180 (6) Å] and N(6)–N(7) [1.161 (7) Å] bond lengths appear longer than the corresponding distances found in the py analogue (Clearfield *et al.*, 1978), which are 1.155 (6) and 1.126 (7) Å, respectively. On the other hand, the difference between the long and short N–N bonds is similar in PPh_3 (0.019 Å) and in py (0.029 Å) derivatives. These values suggest that the resonance form (b) should give a greater contribution to the ground state than the (a) form in both cases.



The Co–N–N [120.4 (3)°] and N–N–N [177.6 (6)°] angles are not far from those reported for the corresponding py derivative, which are 122.0 (5) and 174.7 (7)°.

The structural results of (II) confirm the previous suggestion, based on ^1H NMR spectra (Beck *et al.*, 1982), that the 4,5-bis(methoxycarbonyl)-1,2,3-triazolate ligand binds symmetrically to cobalt through its central N atom. Fig. 2 shows the orientation of the triazole ring with respect to the $(\text{DH})_2$ ligands, which fold along a line nearly parallel to the ring plane. An orientation of the tetrazole ring nearly normal to that

folding line was found in (5-CF₃-tetrazolate)Co(DH)₂-PBU₃ⁿ (Takach, Holt, Alcock, Henry & Nelson, 1980) and was attributed to a positive or non-bonded attraction between the tetrazole N atoms and the C atoms of the five-membered ring of the DH unit. Present results do not give support to this hypothesis, the orientation of the triazole ring being very close to that found in pyridine derivatives (Clearfield *et al.*, 1978). We note that substitution of N₃ by the more bulky triazole derivative provokes a decrease of the Co displacement from the coordination plane and of the bending angle α as well as an increase of the P—Co—N (axial) angle (Table 3). Similar variations have already been observed (Bresciani-Pahor *et al.*, 1980) in other cobaloximes, containing PPh₃, when the methyl group in the axial position is replaced by the bulky neopentyl group.



The Co—P bond is significantly lengthened from 2.311 (1) in (I) to 2.333 (1) Å in (II), suggesting that triazole derivatives exert a *trans* influence which is stronger than that of the azide. This parallels the observed tendency for formation of five-coordinate species in triazolate compounds (Beck *et al.*, 1982).

Acta Cryst. (1984). C40, 746–748

Structure of *trans*-Bis(dimethylphenylphosphine)bis(pyrazole)platinum, [Pt(C₃H₄N₂)₂]{P(CH₃)₂(C₆H₅)₂}]₂

By J. D. OLIVER,* D. F. MULLICA, DAVID A. GROSSIE, W. O. MILLIGAN AND H. O. PERKINS

Departments of Chemistry and Physics, Baylor University, Waco, Texas 76798, USA

(Received 16 September 1983; accepted 7 December 1983)

Abstract. $M_r = 607.55$, monoclinic, $C2/c$, $a = 21.509$ (6), $b = 6.290$ (2), $c = 17.934$ (4) Å, $\beta = 102.54$ (2)°, $V = 2368.7$ Å³, $Z = 4$, $D_m = 1.70$, $D_x = 1.70$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 6.13$ mm⁻¹, $F(000) = 1192$, $T = 291$ K. Final $R = 0.028$ for 1416 unique observed reflections. The Pt atom lies on a crystallographic inversion center with a *trans* arrangement of the dimethylphenylphosphine and pyrazole ligands. The plane of the pyrazole ring forms an angle of 73.8° with the square-planar coordination

The bond lengths (Table 3) and the planarity of the triazole ring, from which the Co is displaced by only 0.02 (4) Å, suggest a delocalization over the ring atoms (form *c*). However, a contribution from the localized form (*d*) cannot be ruled out.

This work has been supported in part by a grant from CNR, Rome (to LR).

References

- BECK, W., NELSON, J. H., TAKACH, N. E., KEMMERICH, T., BOEHME, H. & JABLONSKI, B. (1982). *Inorg. Chem.* **21**, 1226–1232.
- BRESCIANI-PAHOR, N., CALLIGARIS, M. & RANDACCIO, L. (1980). *Inorg. Chim. Acta*, **39**, 173–179.
- BRESCIANI-PAHOR, N., RANDACCIO, L., TOSCANO, P. J. & MARZILLI, L. G. (1982). *J. Chem. Soc. Dalton Trans.* pp. 567–572.
- BRESCIANI-PAHOR, N., RANDACCIO, L., TOSCANO, P. J., SANDERCOCK, A. C. & MARZILLI, L. G. (1982). *J. Chem. Soc. Dalton Trans.* pp. 129–134.
- BRÜCKNER, S. & RANDACCIO, L. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1017–1022.
- CLEARFIELD, A., GOPAL, R., KLINE, R. J., SIPSKI, M. L. & URBAN, L. O. (1978). *J. Coord. Chem.* **8**, 5–13.
- MARZILLI, L. G., TOSCANO, P. J., RAMSDEN, J. H., RANDACCIO, L. & BRESCIANI-PAHOR, N. (1982). *Adv. Chem. Ser.* **196**, 85–99.
- MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169–1175.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY system. Univ. of Maryland, College Park, MD.
- TAKACH, E., HOLT, E. M., ALCOCK, N. W., HENRY, R. A. & NELSON, J. H. (1980). *J. Am. Chem. Soc.* **102**, 2968–2979.

* Present address: The Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45247, USA.