CROATICA CHEMICA ACTA CCACAA **57** (4) 433—441 (1984)

CCA-1457

YU ISSN 0011—1643
UDC 546.733
Original Scientific Paper

Steric Influences in Octahedral Cobaloximes. The Crystal and Molecular Structure of *trans*-methylbis(dimethylglyoximato) (phosphite)cobalt(III) Complexs with Phosphite = $P(OMe)_2Ph$ and $P(OMe)Ph_2$*

Nevenka Bresciani-Pahor, John D. Orbell, and Lucio Randaccio

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

Received May 19, 1983

The crystal structures of the title compounds, $(P(OMe)_2Ph)$-$Co(DH)_2Me$ (*I*) and $(P(OMe)Ph_2)Co(DH)_2Me$ (*II*), are reported. Compound *I* crystallizes in the orthorhombic system, space group *Pbca*, with cell parameters a = 14.652(7), b = 26.45(1) and c = 11.330(6) Å and Z = 8; compound *II* crystallizes in the monoclinic system, space group $P2_1$ with cell parameters a = 9.423(7), b = 15.184(8), c = 8.948 (7) Å and β = 100.50(9)°, Z = 2. Both structures were solved by conventional Patterson and Fourier methods and refined by the block diagonal least-squares method to final *R* values of 0.033(*I*) and 0.034(*II*), using 2108 for *I* and 2063 for *II* independent reflections with $I > 3\sigma(I)$. In both compounds the cobalt atom has a distorted octahedral geometry, the two DH units occupying the equatorial positions and Me and the P-ligand the axial ones. The Co—C and Co—P bond lengths are 2.013(5) and 2.287(1) Å in *I* and 2.019(6) and 2.352(1) Å in *II*, respectively. Linear correlation between Co—P bond lengths and Tolman's cone angles in the series $R_3PCo(DH)_2Me$ is found, with the exception of the $P(OMe)Ph_2$ derivative. Furthermore, the linear relationship between the above Co—P distances and those reported for analogous chloro-derivatives, already found for phosphines, is valid for *I* but not for *II*.

INTRODUCTION

Octahedral cobaloximes, $LCo(III)(DH)_2X$, where DH = monoanion of dimethylglyoxime, L = neutral basic ligand an X = negative ligand, have been proposed[1] and studied[2] as models of the vitamin B_{12} group. Changes in structure and in chemical behaviour, deriving from variation of steric and electronic properties of axial ligands, may give indication on the behaviour of the more complex B_{12} system. Previous structural and spectroscopic studies[3,6] have shown that P-donor ligands, in addition to electronically originated changes, are able to provoke distortions in cobaloximes. Particularly, it has been shown[4] that in the series $(PR_3)Co(DH)_2X$ with X = Cl, Me and R = OMe, Me, Bu, Ph, cyclo-C_6H_{11}, the Co—P bond length increases with increasing bulk of the phosphine and correlates linearly with Tolman's cone angles[7]. In addition, it was observed

---

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

that the lengthening due to the greater trans-influencing ability of Me, as compared with that of Cl is not influenced by the bulk of the phosphine. In fact, a linear relationship (with a slope ~ 1) appeared to correlate the Co—P distances in the $PR_3Co(DH)_2Me$ series with those in the analogous series $PR_3Co(DH)_2Cl$. Since NMR measurements on such compounds indicated that phosphites show differences[8] when compared with phosphines, it was of interest to extend the above structural investigation to cobaloximes containing ligands such as $P(OMe)_2Ph$ and $P(OMe)Ph_2$. Since the structure of the chloro-derivatives has already been determined[6], we report the X-ray structure of the methyl analogues, $(P(OMe)_2Ph)Co(DH)_2CH_3$ (I) and $(P(OMe)Ph_2Co(DH)_2CH_3$ (*II*).

EXPERIMENTAL

Crystal Data and Data Collection. — The cell parameters were determined from precession and Weissenberg photographs and refined on a SIEMENS AED single crystal diffractometer. Crystal data are given in Table I. One check reflection intensity, during the collection of diffraction data for both complexes, was measured every 100 reflections and did not show any systematic variation throughout the data recording. The intensities for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors but not for absorption, owing to the small size of the used crystals and low value of the absorption coefficient.

TABLE I

Crystallographic Data for Compounds I *and* II

Formula	$C_{17}H_{28}CoN_4O_6P$	$C_{22}H_{30}CoN_4O_5P$
M	474.4	520.5
a (Å)	14.652(7)	9.423(7)
b (Å)	26.45(1)	15.184(8)
c (Å)	11.330(6)	8.948(7)
β (°)		100.50(9)
Dm (g/cm³)	1.43(1)	1.36(1)
Dg (g/cm³)	1.44	1.37
Z	8	2
Space group	Pbca	$P2_1$
μ (cm⁻¹)	7.0	6.8
Cryst. dimension (cm³)	0.04×0.03×0.05	0.02×0.03×0.02
No. reflections ($I > 3\sigma(I)$)	2108	2063
2ϑ max (°)	56	56
R	0.033	0.034

Solution and Refinement of Structures. — Both structures were solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares methods. The final cycles were carried out including all hydrogen atom contributions at calculated positions held constant at $B = 5$ Å² and anisotropic temperature factors for all non-hydrogen atoms. The final R values were 0.033 for *I* and 0.034 for *II*. The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$ where $A = 23.2$ and $B = 0.008$ for *I* and $A = 8.9$ and $B = 0.016$ for *II* were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $(\sin\vartheta)/\lambda$. Atomic scattering factors were those given in ref. 9. All the calculations

TABLE II

Atomic Positional Parameters ($\times 10^4$) *for* I *with Estimated Standard Deviations in* Parentheses

	X	Y	Z
Co	1630(0)	1381(0)	1051(0)
P	496(1)	1231(0)	—291(1)
O(1)	2074(3)	2326(1)	—23(3)
O(2)	237(2)	413(1)	539(3)
O(3)	1254(2)	444(1)	2189(3)
O(4)	993(2)	2360(1)	1648(3)
O(5)	—84(2)	758(1)	150(3)
O(6)	—231(2)	1662(1)	—639(3)
N(1)	2223(3)	1823(1)	—5(3)
N(2)	2375(2)	904(1)	277(3)
N(3)	1096(2)	946(1)	2168(3)
N(4)	954(2)	1862(1)	1895(3)
C(1)	3310(4)	1919(2)	—1652(5)
C(2)	2808(3)	1616(2)	—738(4)
C(3)	2895(3)	1076(2)	—560(4)
C(4)	3510(4)	743(2)	—1299(4)
C(5)	2(3)	846(2)	3789(4)
C(6)	537(3)	1150(2)	2915(3)
C(7)	484(3)	1699(2)	2792(4)
C(8)	—18(4)	2046(2)	3600(5)
C(9)	2639(3)	1492(2)	2230(4)
C(10)	—879(4)	571(2)	—469(5)
C(11)	—835(3)	1882(2)	229(4)
C(12)	879(3)	1082(2)	—1774(3)
C(13)	1046(3)	1467(2)	—2575(4)
C(14)	1430(4)	1352(2)	—3669(4)
C(15)	1640(4)	867(3)	—3984(5)
C(16)	1461(4)	484(2)	—3181(5)
C(17)	1083(4)	584(2)	—2073(4)

TABLE III

Atomic Positional Parameters ($\times 10^4$) *for* II *with Estimated Standard Deviations in Parentheses*

	X	Y	Z
Co	2513(1)	2500(0)	1690(1)
P	3237(1)	2732(1)	4317(2)
O(1)	1306(5)	856(3)	2263(5)
O(2)	5191(4)	2864(3)	758(5)
O(3)	3624(5)	4155(3)	864(5)
O(4)	—303(4)	2140(3)	2283(6)
O(5)	2440(4)	2077(3)	5364(5)
N(1)	2454(5)	1276(3)	1955(6)
N(2)	4317(5)	2247(3)	1235(5)
N(3)	2496(5)	3723(3)	1237(5)
N(4)	608(4)	2766(4)	1933(5)
C(1)	3779(9)	—136(5)	1900(10)
C(2)	3636(7)	851(4)	1739(7)
C(3)	4727(7)	1425(4)	1319(7)
C(4)	6118(8)	1115(5)	917(9)
C(5)	1067(9)	5108(5)	917(10)
C(6)	1284(6)	4149(4)	1290(7)
C(7)	171(6)	3583(5)	1691(7)
C(8)	—1319(7)	3883(6)	1784(9)
C(9)	1717(7)	2297(5)	—534(7)
C(10)	2898(9)	1177(4)	5651(8)
C(11)	5114(5)	2727(3)	5289(6)
C(12)	5423(6)	2648(4)	6873(6)
C(13)	6853(6)	2641(4)	7637(6)
C(14)	7973(6)	2690(5)	6845(7)
C(15)	7673(6)	2738(5)	5276(7)
C(16)	6239(6)	2799(4)	4499(6)
C(17)	2591(6)	3780(4)	4931(6)
C(18)	1412(7)	3831(5)	5636(8)
C(19)	876(9)	4661(6)	5993(10)
C(20)	1512(9)	5408(6)	5601(10)
C(21)	2723(9)	5374(5)	4903(10)
C(22)	3266(8)	4565(4)	4551(9)

were done using the computer programs from X-Ray '70. Final positional parameters of non hydrogen atoms are given in Tables II and III. Hydrogen atom coordinates, anisotropic thermal parameters, calculated and observed structure factors are available from the authors.

RESULTS AND DISCUSSION

Description of the Structures. — The numbering scheme for the atoms of *I* and *II* is shown in Figure 1 and 2. Relevant bond lengths and angles are given in Table IV.

In compound *I*, the four N-donors of the $(DH)_2$ moiety are coplanar within ± 0.004 Å and the cobalt atom is displaced by 0.06 Å above their mean plane towards the P atom. The two DH units make an interplanar angle of 4.8°. The corresponding figures for *II* are ± 0.005 Å, 0.09 Å and 8.8°, respectively. The P—Co—CH_3 fragment of *I* is characterized by Co—P, Co—C bond lengths and P—Co—C bond angle of 2.287(1) Å, 2.013(5) Å and 178.4(2)° respectively, whereas in *II* the corresponding figures are 2.352(1), 2.019(6) Å and 175.1(2)° respectively. The other bond lengths and angles are quite normal for such compounds.[3-6] The orientation of the P-ligand with respect to the equatorial $(DH)_2$ ligand for *I* and *II* is shown in Figures 1 and 2 respectively.

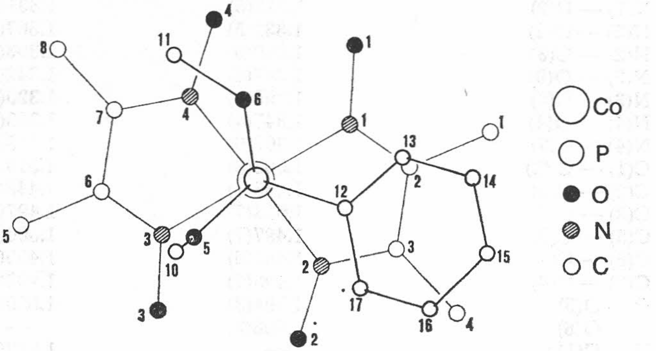

Figure 1. Numbering scheme for the atoms of compound *I*. The orientation of the P-ligand with respect to the equatorial unit is also shown. The C(9) atom of the axial CH_3 group is obscured.

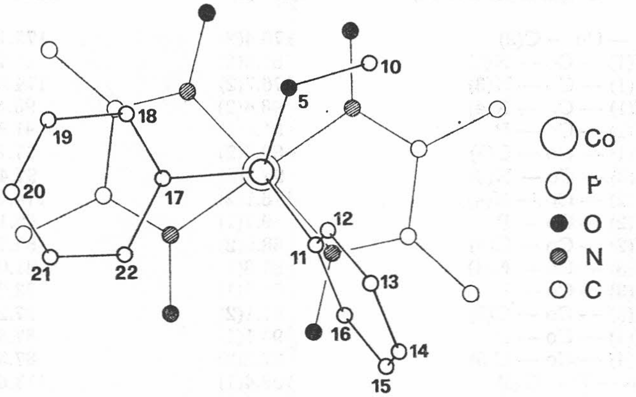

Figure 2. Numbering scheme for the atoms of the P-ligand of compound *II*. Its orientation with respect to the equatorial ligand is also shown. The $CH_3Co(DH)_2$ unit has the same numbering scheme as compound *I*.

TABLE IV

Bond Lengths (Å) and Selected Bond Angles (°) for Compounds I *and* II

	I	*II*
Co — P	2.287(1)	2.352(1)
Co — C(9)	2.013(5)	2.019(6)
Co — N(1)	1.885(4)	1.876(5)
Co — N(2)	1.885(3)	1.859(5)
Co — N(3)	1.881(3)	1.900(5)
Co — N(4)	1.875(3)	1.891(4)
N(1) — O(1)	1.351(5)	1.327(7)
N(1) — C(2)	1.313(6)	1.331(8)
N(2) — O(2)	1.332(5)	1.367(6)
N(2) — C(3)	1.300(6)	1.303(8)
N(3) — O(3)	1.347(4)	1.342(7)
N(3) — C(6)	1.295(5)	1.320(8)
N(4) — O(4)	1.347(4)	1.355(7)
N(4) — C(7)	1.302(6)	1.313(9)
C(1) — C (2)	1.503(8)	1.510(9)
C(2) — C(3)	1.446(7)	1.448(9)
C(3) — C(4)	1.513(7)	1.497(11)
C(5) — C(6)	1.497(7)	1.500(10)
C(6) — C(7)	1.463(6)	1.450(9)
C(7) — C(8)	1.490(7)	1.493(10)
P — O(5)	1.594(3)	1.639(5)
P — O(6)	1.608(3)	—
P — C(11)	—	1.823(5)
P — C(12)	1.815(4)	—
P — C(17)	—	1.824(6)
O(5) — C(10)	1.446(7)	1.442(8)
O(6) — C(11)	1.446(6)	—
C — C (phenyl, mean)	1.387(8)	1.392(11)
P — Co — C(9)	178.4(2)	175.1(2)
N(1) — Co — N(2)	81.5(2)	82.7(2)
N(1) — Co — N(3)	176.7(2)	174.9(2)
N(1) — Co — N(4)	98.4(2)	98.4(2)
N(1) — Co — P	91.1(1)	91.8(2)
N(1) — Co — C(9)	89.6(2)	87.7(3)
N(2) — Co — N(3)	98.3(2)	97.4(2)
N(2) — Co — N(4)	176.1(2)	174.1(2)
N(2) — Co — P	89.7(1)	98.1(1)
N(2) — Co — C(9)	88.9(2)	86.7(2)
N(3) — Co — N(4)	81.6(1)	81.0(2)
N(3) — Co — P	92.3(1)	93.2(1)
N(3) — Co — C(9)	87.1(2)	87.2(3)
N(4) — Co — P	94.1(1)	87.8(1)
N(4) — Co — C(9)	87.2(2)	87.5(2)
Co — P — O(5)	108.4(1)	113.6(2)
Co — P — O(6)	121.5(1)	—
Co — P — C(11)	—	123.8(2)
Co — P — C(12)	115.4(1)	—
Co — P — C(17)	—	112.3(2)
O(5) — P — O(6)	106.2(2)	—
O(5) — P — C(11)	—	103.3(2)
O(5) — P — C(12)	106.5(2)	—
O(5) — P — C(17)	—	98.3(3)
O(6) — P — C(12)	97.6(2)	—
C(11) — P — C(17)	—	102.0(2)

DISCUSSION

Comparison of the Co—P distance of the present compounds with that of the analogous chloro-derivatives[6], $(P(OMe)_2Ph)Co(DH)_2Cl$ (2.213(2) Å) and $(P(OMe)Ph_2)Co(DH)_2Cl$ (2.242(2) Å), shows the expected lengthening of about 0.1 Å due to *trans*-influence of the methyl group which is larger than that of the chloro atom.

Furthermore, the difference of 0.065 Å between the Co—P distances in the methyl derivatives corresponds to the difference of 0.029 Å in the analogous chloro-derivatives. In contrast, the Co—CH_3 bond lengths have nearly the same value in *I* and *II* and do not differ from other values reported for $R_3PCo(DH)_2Me$ complexes, with range from 2.011(3)[3] to 2.026(6) Å[11]. Thus, the present results support previous findings that the Co—Me bond length is not significantly influenced by the bulk and the nature of the *trans* P-ligand. On the contrary, the present Co—P distances agree with the previous observation[3] that in the series $(R_3P)Co(DH)_2X$ (X = Cl and Me), the Co—P bond lengths increase with increasing bulkiness of the PR_3 ligand, i. e. with increasing Tolman's cone angle. In Figure 3 a plot of the Co—P distances in the methyl derivatives

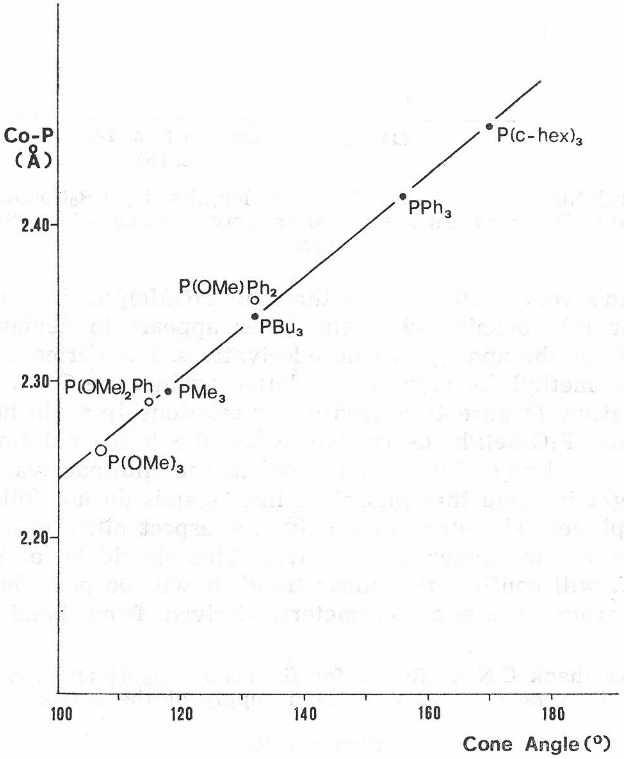

Figure 3. Plot of Co—P bond lengths in $PR_3Co(DH)_2Me$ against Tolman's cone angles. For PPh_3 a cone angle of 156° has been assumed[6]. In the PBu_3 derivative, the *trans* ligand is —C_5H_4N instead of Me. The diameter of the circle is twice the e.s.d. of each distance. Full circles represent phosphine ligands and open circles represent the others.

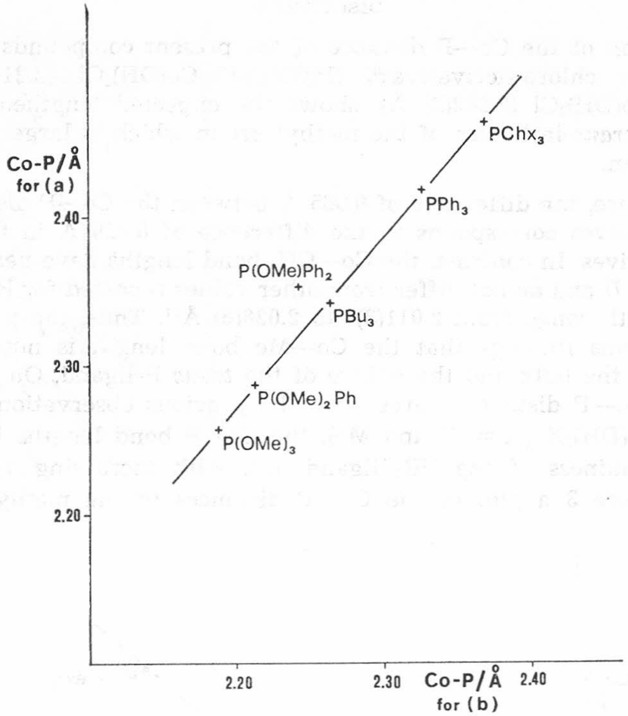

Figure 4. Correlation between Co—P bond lengths in $PR_3Co(DH)_2Me$ (a) and $PR_3Co(DH)_2Cl$ (b). Twice e.s.d.'s are approximately represented by the arms of the crosses.

against Tolman's cone angles shows that the $P(OMe)_2Ph$ derivative fits well into the linear relationship, while the other appears to deviate slightly, as already found[6] for the analogous chloroderivatives. Furthermore, if the Co—P bond lengths in methyl derivatives are plotted against the Co—P bond lengths in chloroderivatives (Figure 4), a good linear relationship again holds, with the exception of the $P(OMe)Ph_2$ derivative. Since the latter exhibits the largest deviation from the line of Figure 3, as well as the chloroderivative analogue[6], this result might indicate that phosphite like ligands do not follow the linear trend of phosphines. Therefore to clarify this aspect other cobaloximes, containing phosphites, are under investigation. This should be of interest, since if further data will confirm the linear trend, it will be possible to obtain an experimental scale of steric parameters, derived from bond length measurements.

The authors thank C.N.R. (Rome) for financial support and Dr. P. J. Toscano, North Western University (U.S.A.) for kind supply of the crystals.

REFERENCES

1. G. N. Schrauzer and R. G. Windgassen, *J. Amer. Chem. Soc.* **88** (1966) 3738 and references therein.
2. G. Costa, G. Tauzher, and A. Puxeddu, *Inorg. Chim. Acta* **3** (1969) 41 and references therein; P. J. Toscano and L. G. Marzilli, *Inorg. Chem.* **18** (1979) 421 and references therein; K. L. Brown and A. W. Awtrey,

Inorg. Chem. **17** (1978) 111 and references therein; F. T. T. Ng, G. L. Rempel, and J. Halpern, *J. Amer. Chem. Soc.* **104** (1982) 621 and reference therein; W. D. Hemphill and D. G. Brown, *Inorg. Chem.* **16** (1977) 766; N. Bresciani-Pahor, L. Randaccio, M. Summers, and P. J. Toscano, *Inorg. Chim. Acta* **68** (1983) 69 and references therein.

3. N. Bresciani-Pahor, M. Calligaris, and L. Randaccio, *Inorg. Chim. Acta* **39** (1980) 173.
4. L. G. Marzilli, P. J. Toscano, J. H. Ramsden, L. Randaccio, and N. Bresciani-Pahor, *Adv. Chem. Ser.* **196** (1982) 86 and references therein.
5. N. Bresciani-Pahor, L. Randaccio, P. J. Toscano, A. C. Sandercock and L. G. Marzilli, *J. Chem. Soc. Dalton Trans.* (1982) 129.
6. N. Bresciani-Pahor, L. Randaccio, and P. J. Toscano, *J. Chem. Soc. Dalton Trans.* (1982) 1559.
7. C. A. Tolman, *Chem. Rev.* **77** (1977) 313.
8. J. A. Kargol, R. W. Crecely, J. L. Burmeister, P. J. Toscano, and L. G. Marzilli, *Inorg. Chim. Acta* **40** (1980) 79.
9. F. H. Moore, *Acta Crystallogr.* **16** (1963) 1169.
10. J. M. Stewart, F. A. Kundal, J. C. Baldwin, *X-Ray System of Programs*, University of Maryland, MD, 1970.
11. N. Bresciani-Pahor, M. Calligaris, L. Randaccio, and L. G. Marzilli, *Inorg. Chim. Acta* **32** (1979) 181.

SAŽETAK

Sterički utjecaji u oktaedarskim kobaloksimima. Kristalna i molekulska struktura *trans*-metilbis(dimetilglioksimato) (fosfit)kobalt(III) kompleksa sa fosfit = P (OMe)$_2$Ph i P (OMe)Ph$_2$.

Nevenka Bresciani-Pahor, John D. Orbell i Lucio Randaccio

Prikazana je kristalna struktura spojeva (P(OMe)$_2$Ph)Co(DH)$_2$Me (*I*) i (P(OMe)-Ph$_2$Co(DH)$_2$Me (*II*). Spoj (*I*) kristalizira u rompskom sustavu, prostorna grupa *Pbca*, s parametrima ćelije $a = 14{,}652(7)$, $b = 26{,}45(1)$, $c = 11{,}330(6)$ Å, $Z = 8$; spoj (*II*) kristalizira u monoklinskom sustavu, prostorna grupa $P2_1$, s parametrima ćelije $a = 9{,}423(7)$, $b = 15{,}184(8)$, $c = 8{,}948(7)$ Å i $\beta = 100{,}50(9)^\circ$, $Z = 2$. Obje strukture riješene su metodama Pattersona i Fouriera, a utočnjene metodom najmanjih kvadrata do vrijednosti *R* od 0,033 (*I*) i 0,034 (*II*) sa 2108 za (*I*) i 2063 neovisnih refleksa za (*II*). Koordinacijski poliedar oko atoma kobalta u oba je spoja deformirani oktaedar sa dvije DH-jedinice u ekvatorijalnom, a s Me i P-ligandom u aksijalnom položaju. Duljine veza Co—C i Co—P iznose 2,013(5) i 2,287(1) Å u (*I*), a 2,019(6) i 2,352(1) Å u spoju (*II*). Nađen je linearni odnos između duljina veza Co—P i kuteva Tolmanova stošca u serijama R$_3$PCo(DM)$_2$Me s izuzetkom derivata P(OMe)Ph$_2$. Osim toga, nađen je linearni odnos između razmaka Co—P u (*I*) i u već objavljenom analognom klorderivatu. U slučaju (*II*) taj odnos ne vrijedi.