Synthesis of Ylide Complexes of Cobalt and the Crystal Structure of [Benzoyl(1-pyridinio)methanide]chlorobis(dimethylglyoximato)cobalt(III) Toluene Solvate

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Bis(dimethylglyoximato)halogenocobalt(III) complexes of benzoyl(1-pyridinio)methanide were synthesized by a new kind of oxidative addition reaction of *N*-phenacylpyridinium halides to diaquabis(dimethylglyoximato)cobalt-(II) in air. The crystal structure of the [benzoyl(1-pyridinio)methanide]chlorobis(dimethylglyoximato)cobalt(III) toluene solvate was solved by single-crystal X-ray diffraction techniques. The crystals are monoclinic (space group $P2_1/c$), with cell dimensions of $a=11.41(1)$, $b=10.28(1)$, $c=27.50(3)$ Å, $\beta=116.3(1)°$, and $Z=4$. The final R was 0.068. The ylide ligand coordinates to cobalt through the ylide carbon, with a Co–C distance of 2.07(1) Å, and the chlorine atom is bonded to cobalt with a Co–Cl distance of 2.285(4) Å and with a C(ylide)–Co–Cl bond angle of 175.5(3)°. The dimethylglyoxime ligands and cobalt atom are co-planar to within 0.04 Å.

We have long been interested in the nature of ylide as ligands,[1] and we reported recently the synthesis of chelating ylide ligands and their palladium and platinum complexes.[2] Ylides are formally similar to such neutral ligands as amines or phosphines, but in another respect the ylide carbon-metal bonding formed upon coordination resembles the metal-carbon bond of metal alkyls. Because of this dual function, it seemed intriguing to synthesize ylide complexes of cobaloxime, which is known to form a wide variety of ER_3 (E=N or P) as well as alkyl (E=C) complexes,[3] and to gain insight into the nature of the ylide carbon-metal bonding. Thus, we have succeeded in the preparation of benzoyl-(1-pyridinio)methanide complexes of cobaloxime by a new type of oxidative addition reaction starting from the corresponding *N*-phenacylpyridinium halides; the structures were inferred from the infrared and ^{1}H NMR spectra.[4] In the present study, the crystal structure of the [benzoyl(1-pyridinio)methanide]chlorobis(dimethylglyoximato)cobalt(III) toluene solvate was determined by X-ray diffraction techniques, and the bonding of the ylide carbon to cobalt was confirmed.

Experimental

Synthesis. $[Co(dmgH)_2(H_2O)_2]$ (dmgH=dimethylglyoxime mono anion)[5] (6.5 g) and *N*-phenacylpyridinium chloride (4.2 g) were suspended in 99% ethanol (50 ml), and air was bubbled into the suspension for 30 min at 10 °C. The mixture became homogeneous, and then a brown solid was precipitated. The product was filtered, washed with ethanol (30 ml) and diethyl ether (30 ml), and dried *in vacuo*, (4.5 g). The infrared spectrum of the crude product indicated that it contained about 20% of $[pyCH_2COC_6H_5]^+[CoCl_2(dmgH)_2]^-$ (ν(CO) 1690 cm^{-1}) (py=pyridine). The product was dissolved in CH_2Cl_2 (250 ml), and diethyl ether (100 ml) was added very slowly to produce very fine crystals of $[CoCl(dmgH)_2(pyCHCOC_6H_5)]$, (2.5 g). $[CoBr(dmgH)_2(pyCHCOC_6H_5)]$ and $[CoI(dmgH)_2(pyCHCOC_6H_5)]$ were prepared in a similar fashion. The properties of these complexes are given in Table 1.

Preparation of the Crystal. $[CoCl(dmgH)_2(pyCHCOC_6H_5)]$ (0.5 g) was dissolved in warm CH_2Cl_2 (50 ml), and then toluene (30 ml) was slowly added and then filtered out. The solution was kept overnight at 5 °C, and the black crystals thus precipitated were filtered, washed with diethyl ether (10 ml), and dried. The ^{1}H NMR spectrum indicated that the crystals contained one mole toluene per mole of the complex.

Found: C, 54.7; H, 5.6; N, 11.4; Cl, 6.2%. Calcd for $C_{28}H_{33}ClCoN_5O_5$: C, 54.8; H, 5.4, N, 11.4; Cl, 5.8%.

Crystal Data. A single crystal with dimensions of *ca.* $0.45\times0.25\times0.15$ mm was used for the measurements of the diffraction intensities and unit-cell dimensions on a Rigaku automated four-circle diffractometer, by the use of graphite-monochromatized Mo $K\alpha$ radiation. The unit-cell constants were obtained by a least-squares refinement of the angular measurements of 25 reflections, but the results were not always satisfactory because of the weak intensities of the high-angle reflections.

$C_{21}H_{25}ClCoN_5O_5\cdot C_7H_8$, M=613.7, monoclinic, space group $P2_1/c$ from systematic absences: $h0l$, $l=2n+1$, $0k0$, $k=2n+1$. $a=11.14(1)$, $b=10.28(1)$, $c=27.50(3)$ Å, $\beta=116.3(1)°$, $V=2825$ Å^3, $Z=4$, $D_m=1.44$ g cm^{-3}, $D_x=1.44$ g cm^{-3}, $\mu=7.74$ cm^{-1} (Mo $K\alpha$), Mo $K\alpha$ radiation $\lambda=0.7107$ Å.

Data Collection. The intensity data were recorded by the ω-2θ scan technique, with a scan speed of 2° min^{-1}; background counts over 10 s were taken at each end of the scan. The intensities of 3 standard reflections measured every 50 reflections during the data collection did not vary by more than 4%. The intensities were measured up to 2θ 60°, and 1997 independent reflections with $F_o>3\sigma$ were used for the structure analysis. The data were corrected for Lorentz and polarization effects, but not for absorption.

Solution and Refinement of the Structure. The structure

Table 1. Elemental analysis, infrared, and ^{1}H NMR spectral properties of $[CoX(dmgH)_2(pyCHCOC_6H_5)]$

X	Elemental analysis Found (Calcd)%				IR(KBr) ν(CO) cm^{-1}	^{1}H NMR(CH_3CN) δ(CH) ppm
	C	H	N	X		
Cl	48.5(48.3)	4.9(4.8)	13.3(13.4)	6.6(6.8)	1654	5.62
Br	44.3(44.5)	4.4(4.5)	12.4(12.4)	14.9(14.1)	1641	5.55
I	40.5(41.1)	4.4(4.1)	11.5(11.4)		1640	5.60

was solved by the usual heavy-atom method. The position of the cobalt atom was determined from a Patterson synthesis, and all the non-hydrogen atoms were located by the subsequent Fourier syntheses. The positions of the atoms were refined by the block-diagonal least-squares method with anisotropic temperature factors. A difference-Fourier synthesis at the stage of $R=0.083$ revealed the positions of the ylide methine hydrogen, 13 aromatic hydrogens, and one hydrogen for each of the methyl groups of the dimethylglyoxime ligands, but no hydrogen atom was located for the methyl group of the toluene molecule or for the oxime groups. Further refinements including the calculated positions (l(C–H) 1.08 Å, $B=3$ Å^2) of the remaining aromatic hydrogen atoms and the methyl hydrogen atoms of the dimethylglyoxime ligands, using isotropic temperature factors for the hydrogen and anisotropic temperature factors for non-hydrogen atoms, reduced the final R factor to 0.068. The H–C–H and C–C–H bond angles were normal within the estimated standard deviations.

Atomic scattering factors were taken from Ref. 6, those of cobalt and chlorine being corrected for the real and imaginary parts of anomalous dispersion, using values from Ref. 7. A weighting scheme with $w=1$ for $|F_o|\geq 21.80$ on an absolute scale and $w=0.5$ in other cases was employed.

The calculations were performed on the HITAC 8700/8800 computer at the Computer Center of the University of Tokyo, using a local version of the UNICS programs.[8]

Results and Discussion

The present ylide complexes of cobaloxime are formed in the presence of air by the replacement of the two H_2O ligands in $[Co^{II}(dmgH)_2(H_2O)_2]$ with halogen and benzoyl(1-pyridinio)methanide. The reaciton seems to proceed according to the following scheme, although the reaction mechanism is not clear:

$$[Co^{II}(dmgH)_2(H_2O)_2] + [pyCH_2COC_6H_5]^+X^- + 1/4O_2 \longrightarrow [Co^{III}X(dmgH)_2(pyCHCOC_6H_5)] + 5/2H_2O.$$

The addition of halogen and the ylide ligands, which is accompanied by the oxidation of Co(II) to Co(III), may be described as a kind of oxidative addition reaction. This reaction, however, is somewhat different from the ordinary oxidative addition of X–Y molecules to Co(II), which results in the formation of two Co(III) species, such that [Co(II)]+X–Y→[Co(III)X]+[Co(III)Y].[9] The synthesis of ylide complexes directly from onium salts is advantageous because these salts are generally much more stable than the corresponding free ylides, and some palladium ylide complexes from phosphonium salts have been reported.[10] The present synthesis provides another example of the *in situ* synthesis of ylide complexes starting from onium salts.

The infrared spectra of the ylide complexes show ν(CO) at lower wave numbers than the corresponding *N*-phenacylpyridinium halides (*cf.* $[pyCH_2COC_6H_5]^+X^-$: 1693 cm^{-1} (X=Cl), 1695 cm^{-1} (X=Br), 1698 cm^{-1} (X=I), KBr disk); the lowering of ν(CO) is considered to indicate the bonding of the ylide carbon to the metal in keto-stabilized ylide complexes.[2] It has been reported that a platinum pyridinium propylide complex, $[PtCl_2(py)(pyCHCH_2CH_3)]$[11] shows an ylide methine proton signal at δ 5.67 in $CDCl_3$, which is near the positions of the signals of the present cobalt complexes. The methyl-proton signals of the dimethylglyoxime ligands at δ 1.9 are split into two absorptions in an intensity ratio of 1 : 1. This splitting may presumably be ascribed to the different magnetic environments of the methyl groups due to the presence of the asymmetric ylide carbon.[10]

Molecular and Crystal Structure. The numbering scheme employed in this paper is shown in Fig. 1. Figure 2 is a stereoview of the unit cell drawn by ORTEP. The final atomic parameters and their standard deviations are listed in Tables 2 and 3. Table 4 gives the bond distances, and Table 5, the bond angles within the molecule. The least-squares planes, dihedral angles, and vector-plane angles are given in Table 6.*

The results of the structure determination of the [benzoyl(1-pyridinio)methanide]chlorobis(dimethylgly-

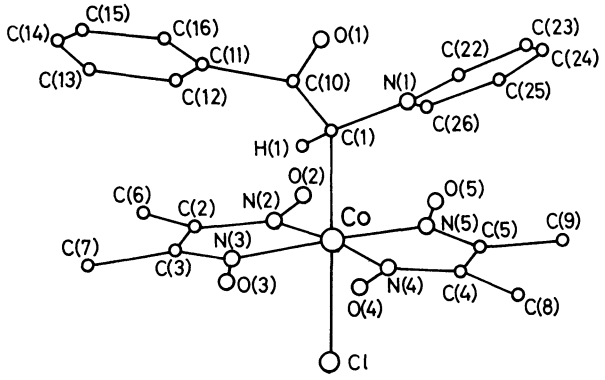

Fig. 1. Molecular structure of $[CoCl(dmgH)_2(pyCHCOC_6H_5)]$ and numbering scheme of atoms. The carbon atoms of toluene are not shown and they are numbered from C(31) to C(37).

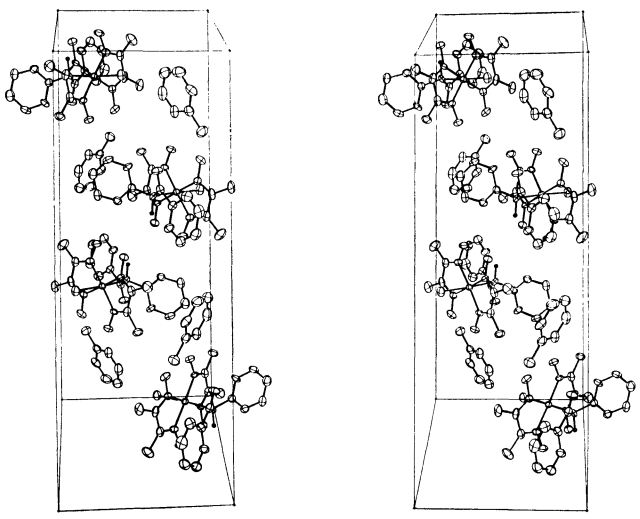

Fig. 2. Stereoview of a unit cell of $[CoCl(dmgH)_2(pyCHCOC_6H_5)]$. The b axis is horizontal to the right, the c axis is vertical, and the a axis is perpendicular coming toward the reader. The thermal ellipsoids are drawn at the 30% probability level (ORTEP).

* The observed and calculated structure factors are held by the office of the Chemical Society of Japan as Document No. 7805.

TABLE 2. ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$) OF THE NON-HYDROGEN ATOMS, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

The U_{ij}'s are defined by: $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	4703(1)	2699(1)	3838(1)	32(1)	34(1)	37(1)	0(1)	18(1)	−1(1)
Cl	6252(3)	1075(3)	4044(1)	46(2)	45(2)	84(2)	6(2)	36(2)	4(2)
N (1)	3848(8)	5487(9)	3589(4)	45(5)	41(6)	55(6)	3(5)	29(5)	−1(5)
N (2)	3396(8)	1535(8)	3377(4)	41(5)	40(5)	53(6)	3(5)	30(5)	2(5)
N (3)	4182(8)	1943(9)	4354(4)	41(5)	52(6)	53(6)	−1(5)	33(5)	0(5)
N (4)	6044(8)	3795(8)	4308(3)	46(5)	38(5)	28(5)	4(5)	19(4)	9(4)
N (5)	5271(8)	3379(8)	3333(3)	44(5)	44(6)	42(6)	2(4)	30(5)	−7(4)
O (1)	1547(7)	4119(8)	2842(3)	57(5)	86(7)	34(5)	−7(5)	16(4)	4(5)
O (2)	3069(7)	1377(8)	2842(3)	54(5)	65(6)	58(5)	−9(5)	26(4)	−28(5)
O (3)	4714(7)	2350(9)	4871(3)	78(5)	75(6)	42(5)	19(5)	36(4)	13(5)
O (4)	6319(7)	3969(7)	4832(3)	56(5)	56(5)	37(5)	−4(4)	14(4)	−7(4)
O (5)	4676(7)	3027(7)	2814(3)	67(5)	64(6)	43(5)	0(0)	32(4)	−12(4)
C (1)	3393(10)	4230(10)	3710(4)	34(6)	35(7)	40(7)	−1(5)	15(5)	15(5)
C (2)	2871(11)	739(11)	3603(5)	36(6)	33(7)	93(10)	3(5)	32(7)	−7(7)
C (3)	3347(10)	1026(11)	4188(5)	43(7)	39(7)	86(10)	9(6)	39(7)	5(7)
C (4)	6771(10)	4392(11)	4116(5)	29(6)	39(7)	76(9)	−5(5)	20(6)	−10(6)
C (5)	6271(10)	4139(10)	3534(5)	34(6)	39(7)	77(9)	−1(5)	29(6)	4(7)
C (6)	1863(12)	−282(12)	3290(6)	59(8)	45(8)	114(12)	−33(7)	45(8)	−19(8)
C (7)	2885(13)	266(15)	4528(6)	66(9)	89(11)	112(13)	3(9)	60(9)	33(10)
C (8)	7896(13)	5292(14)	4436(6)	66(9)	74(10)	89(11)	−19(8)	35(9)	−11(9)
C (9)	6885(12)	4742(13)	3185(5)	68(8)	71(9)	58(8)	−8(8)	42(7)	6(7)
C (10)	2021(11)	3898(11)	3345(5)	47(7)	42(7)	64(8)	−3(6)	25(7)	−9(7)
C (11)	1131(10)	3264(11)	3557(5)	30(6)	49(7)	57(8)	0(5)	21(6)	9(6)
C (12)	1338(11)	3463(12)	4091(5)	57(8)	63(8)	60(8)	7(7)	35(7)	11(7)
C (13)	390(12)	2893(13)	4223(5)	73(8)	65(9)	96(11)	−14(8)	58(8)	−6(8)
C (14)	−638(12)	2130(14)	3886(6)	64(8)	70(9)	97(10)	−1(8)	51(8)	12(9)
C (15)	−826(11)	1945(13)	3367(6)	40(7)	74(10)	104(11)	−25(7)	24(7)	−19(9)
C (16)	67(11)	2521(14)	3187(5)	60(7)	77(10)	67(8)	19(8)	21(7)	8(9)
C (22)	3721(11)	5742(11)	3079(5)	51(7)	57(8)	51(7)	6(6)	33(6)	22(6)
C (23)	4139(11)	6912(12)	2974(5)	61(7)	77(10)	51(8)	27(7)	36(7)	29(7)
C (24)	4701(12)	7820(13)	3384(6)	65(8)	58(8)	98(11)	9(8)	42(8)	4(9)
C (25)	4819(12)	7547(11)	3901(6)	63(7)	41(8)	87(9)	8(7)	34(7)	−1(8)
C (26)	4402(11)	6359(12)	3975(4)	50(7)	52(8)	50(8)	−1(6)	27(6)	−4(6)
C (31)	177(11)	2340(12)	1329(5)	59(7)	57(8)	74(8)	12(8)	38(7)	−6(8)
C (32)	−691(11)	2279(14)	779(5)	47(7)	76(9)	66(8)	18(8)	13(6)	−21(8)
C (33)	−442(16)	2962(16)	406(6)	131(13)	101(13)	75(10)	55(11)	54(10)	14(10)
C (34)	694(16)	3674(15)	553(6)	140(15)	76(11)	98(13)	38(11)	76(12)	21(10)
C (35)	1559(14)	3737(14)	1111(7)	87(11)	52(9)	144(15)	−8(8)	68(11)	−9(10)
C (36)	1333(13)	3078(12)	1489(6)	67(8)	46(8)	93(11)	−8(7)	34(8)	−7(7)
C (37)	−109(15)	1645(15)	1739(6)	114(13)	77(11)	100(13)	4(10)	73(11)	13(9)

oximato)cobalt(III) toluene solvate have proved that the complex is an ylide complex in which the ylide carbon coordinates to cobalt. The Co–C(1) bond length, 2.07 (1) Å, is close to the bond length of Co–C, 2.04 Å, in carbomethoxymethylbis(dimethylglyoximato)(pyridine)-cobalt(III),[12] one of the few alkyl cobaloxime complexes whose crystal structures have been described in the literature.[13] The alkyl moiety, CH_2COOCH_3, is comparable to benzoyl(1-pyridinio)methanide in that both have a carbonyl group adjacent to the carbon which is bonded to cobalt.

The ylide carbon C(1) is bonded to the N(1) of pyridine, the C(10) of the carbonyl group, and H(1) as well as cobalt, and the bond angles, Co–C(1)–N(1) 114.6(8)°, Co–C(1)–C(10) 112.7(7)° and N(1)–C(1)–C(10) 114.4(8)°, are a little larger than the normal tetrahedral angle of 109°28′; the deviation of C(1) from the plane (4) formed by N(1), C(10), and Co is 0.41 Å. The ylide methine hydrogen atom H(1) is clearly evident in the difference-Fourier map.

The cobalt atom and the four nitrogen atoms of the dimethylglyoxime ligands are planar to within 0.04 Å, The Co–N bond distances range from 1.86(1) to 1.92(1) Å, but we are not certain whether the difference of 0.06 Å, about six times the standard deviation, actually reflects the non-equivalence of the Co–N bonds. The Co–Cl bond distance is 2.285(4) Å, and the Cl···Co vector is almost perpendicular (89.2°) to the plane(1)

TABLE 3. ATOMIC COORDINATES ($\times 10^3$) AND ISOTROPIC THERMAL PARAMETERS OF THE HYDROGEN ATOMS, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z	B(Å^2)
H (1)	351 (9)	432 (9)	413 (4)	1 (2)
H (12)	221 (12)	391 (13)	434 (5)	6 (3)
H (13)	53 (9)	324 (10)	450 (4)	2 (2)
H (14)	−130 (12)	174 (13)	407 (5)	6 (4)
H (15)	−148 (9)	134 (9)	304 (4)	1 (2)
H (16)	−11 (13)	263 (15)	286 (5)	8 (4)
H (22)	334 (9)	499 (10)	284 (4)	2 (3)
H (23)	400 (8)	703 (9)	266 (3)	1 (2)
H (24)	504 (11)	874 (12)	340 (4)	5 (3)
H (25)	527 (8)	821 (8)	413 (3)	0 (2)
H (26)	461 (8)	611 (9)	437 (3)	0 (2)
H (32)	−159 (10)	178 (11)	67 (4)	4 (3)
H (33)	−136 (15)	283 (17)	−5 (6)	11 (5)
H (36)	179 (10)	320 (10)	186 (4)	3 (3)
H (61)	159 (12)	−38 (13)	285 (5)	6 (4)
H (71)	221 (13)	−17 (14)	440 (5)	7 (4)
H (81)	801 (9)	558 (10)	475 (4)	2 (3)
H (91)	614 (12)	490 (13)	282 (5)	5 (4)

a) H(mn) is the hydrogen atom bonded to C(mn), while H(61), H(71), H(81), and H(91) are the methyl hydrogen atoms of the dimethylglyoxime ligands.

of the dimethylglyoxime ligands. The C(1)···Co vector is a little out of the perpendicular (85.6°), making the C(1)–Co–Cl bond angle 175.5(3)°. There is no indication that the carbonyl oxygen O(1) forms any significant hydrogen bonding with an oxime hydrogen atom of the dimethylglyoxime ligand, which in [CoCH-$(CH_3)COCH_3(dmgH)_2(py)$] was suspected to account for the lowering of the ν(CO) of the infrared spectra.[14] The C(10)–O(1) bond distance of 1.26 Å indicates an essentially double bond, but the lowering of the ν(CO) of 39 cm^{-1} in the ylide complex compared with that

TABLE 4. BOND LENGTHS (l/Å), WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Co–Cl	2.285 (4)	C (10) – C (11)	1.50 (2)
Co–C (1)	2.07 (1)	C (11) – C (12)	1.40 (2)
Co–N (2)	1.88 (1)	C (12) – C (13)	1.39 (2)
Co–N (3)	1.92 (1)	C (13) – C (14)	1.36 (2)
Co–N (4)	1.86 (1)	C (14) – C (15)	1.36 (2)
Co–N (5)	1.90 (1)	C (15) – C (16)	1.42 (2)
N (2) – O (2)	1.36 (1)	C (16) – C (11)	1.40 (2)
N (3) – O (3)	1.34 (1)	C (31) – C (32)	1.39 (2)
N (4) – O (4)	1.35 (1)	C (32) – C (33)	1.37 (2)
N (5) – O (5)	1.33 (1)	C (33) – C (34)	1.36 (2)
N (2) – C (2)	1.31 (2)	C (34) – C (35)	1.41 (2)
N (3) – C (3)	1.26 (1)	C (35) – C (36)	1.35 (3)
N (4) – C (4)	1.30 (2)	C (36) – C (31)	1.39 (2)
N (5) – C (5)	1.27 (1)	C (31) – C (37)	1.49 (2)
C (2) – C (6)	1.50 (2)	C (12) – H (12)	1.0 (1)
C (3) – C (7)	1.48 (2)	C (13) – H (13)	0.8 (1)
C (4) – C (8)	1.49 (2)	C (14) – H (14)	1.1 (2)
C (5) – C (9)	1.54 (2)	C (15) – H (15)	1.1 (1)
C (2) – C (3)	1.48 (2)	C (16) – H (16)	0.8 (2)
C (4) – C (5)	1.47 (2)	C (22) – H (22)	1.0 (1)
C (1) – C (10)	1.45 (1)	C (23) – H (23)	0.8 (1)
C (1) – H (1)	1.1 (1)	C (24) – H (24)	1.0 (1)
O (2) – O (5) [a]	2.49 (1)	C (25) – H (25)	0.9 (1)
O (3) – O (4) [a]	2.48 (1)	C (26) – H (26)	1.0 (1)
C (10) – O (1)	1.26 (1)	C (32) – H (32)	1.0 (1)
C (1) – N (1)	1.48 (2)	C (33) – H (33)	1.2 (1)
N (1) – C (22)	1.37 (2)	C (36) – H (36)	0.9 (1)
C (22) – C (23)	1.37 (2)	C (6) – H (61)	1.1 (1)
C (23) – C (24)	1.38 (2)	C (7) – H (71)	0.8 (1)
C (24) – C (25)	1.40 (2)	C (8) – H (81)	0.9 (1)
C (25) – C (26)	1.35 (2)	C (9) – H (91)	1.0 (1)
C (26) – N (1)	1.32 (1)		

a) The oxygen atoms are probably bonded through an oxime hydrogen atom.

TABLE 5. BOND ANGLES (ϕ/°), WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

C (1) – Co – Cl	175.5 (3)	C (1) – C (10) – C (11)	120 (1)
N (2) – Co – N (3)	80.9 (4)	C (12) – C (11) – C (16)	122 (1)
N (3) – Co – N (4)	98.3 (4)	C (22) – N (1) – C (26)	120 (1)
N (4) – Co – N (5)	81.9 (4)	C (32) – C (31) – C (36)	118 (1)
N (5) – Co – N (2)	98.8 (4)	O (2) – N (2) – C (2)	118 (1)
Co – N (2) – C (2)	117.0 (9)	O (3) – N (3) – C (3)	122 (1)
Co – N (3) – C (3)	117.0 (9)	O (4) – N (4) – C (4)	119 (1)
Co – N (4) – C (4)	117.1 (9)	O (5) – N (5) – C (5)	124 (1)
Co – N (5) – C (5)	115.0 (9)	N (2) – C (2) – C (3)	112 (1)
Co – N (2) – O (2)	124.2 (7)	N (3) – C (3) – C (2)	113 (1)
Co – N (3) – O (3)	121.4 (7)	N (4) – C (4) – C (5)	111 (1)
Co – N (4) – O (4)	123.8 (7)	N (5) – C (5) – C (4)	115 (1)
Co – N (5) – O (5)	121.0 (7)	C (3) – C (2) – C (6)	125 (1)
Co – C (1) – N (1)	114.6 (8)	C (2) – C (3) – C (7)	122 (1)
Co – C (1) – C (10)	112.7 (7)	C (5) – C (4) – C (8)	125 (1)
Co – C (1) – H (1)	98 (6)	C (4) – C (5) – C (9)	123 (1)
N (1) – C (1) – C (10)	114.4 (8)	N (2) – C (2) – C (6)	123 (1)
H (1) – C (1) – N (1)	106 (6)	N (3) – C (3) – C (7)	125 (1)
H (1) – C (1) – C (10)	110 (6)	N (4) – C (4) – C (8)	124 (1)
C (1) – C (10) – O (1)	121 (1)	N (5) – C (5) – C (9)	122 (1)
O (1) – C (10) – C (11)	118 (1)		

Table 6.

(a) Displacements (l/Å) of relevant atoms from least-squares planes[a)]

Plane (1) [N(2), N(3), N(4), N(5)]
$-0.655X + 0.724Y - 0.216Z + 0.434 = 0$
Co 0.04, N(2) 0.00, N(3) 0.00, N(4) 0.00, N(5) 0.00, O(2) −0.02, O(3) 0.05, O(4) 0.07, O(5) 0.03, C(2) −0.15, C(3) −0.12, C(4) −0.13, C(5) −0.11, C(6) −0.25, C(7) −0.26, C(8) −0.20, C(9) −0.21

Plane (2) [N(1), C(22), C(23), C(24), C(25), C(26)]
$0.888X - 0.388Y + 0.249Z + 0.060 = 0$
N(1) −0.01, C(22) 0.01, C(23) 0.00, C(24) 0.00, C(25) −0.01, C(26) 0.01, C(1) −0.01

Plane (3) [C(11), C(12), C(13), C(14), C(15), C(16)]
$0.497X - 0.816Y + 0.293Z + 1.705 = 0$
C(11) 0.00, C(12) 0.01, C(13) −0.02, C(14) 0.01, C(15) 0.00, C(16) −0.01, C(10) −0.06

Plane (4) [N(1), C(10), Co]
$0.409X - 0.101Y - 0.907Z + 8.631 = 0$
C(1) −0.41

(b) Dihedral angles (ϕ/°) between planes
(1)-(2) 23.7, (1)-(3) 11.4

(c) Vector-plane angles (ϕ/°)
Co···Cl-(1) 89.2, Co···C(1)-(1) 85.6

a) The X, Y, and Z coordinates in Å are referred to the crystallographic axes.

of the N-phenacylpyridinium chloride may be associated with the small reduction of the CO bond order in the ylide complex.[15)]

The stereoview of a unit-cell (Fig. 2) shows a crystal packing of the complex with toluene molecules filling the voids enclosed by the molecules of the complex. The toluene molecules probably make a minor contribution to the lattice forces, since the crystals used in the present X-ray analysis were very brittle.

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