Table 4. C–C bond lengths in acetic acid and derivatives

| Compound | C–C | e.s.d. | References |
|---|---|---|---|
| Acetic acid | 1·478 Å | 0·006 Å | Nahringbauer (1970). |
| $CH_3COONH_4.CH_3COOH$ | 1·488 | 0·005 | Nahringbauer (1969). |
| $C_6H_5N_2Cl.CH_3COOH$ | 1·470 | 0·016 | Rømming & Tjørnhom (1968). |
| Propionic acid | 1·502 | 0·01 | Strieter et al. (1962). |
| Glycollic acid | 1·508 | 0·003 | Pijper (1971). |
|  | 1·498 | 0·003 |  |
| Fluoroacetic acid | 1·46 | 0·01 | Present work. |

logues. One short intermolecular contact is worth mentioning, namely the C(4)–H(7)...O(3) $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$ contact, with a C···O distance of 3·36 Å and H···O of 2·29 Å.

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# The Crystal and Molecular Structure of Dicarbonylnitrosyltriphenylphosphinecobalt(0), C20H15CoNO3P

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Dicarbonylnitrosyltriphenylphosphinecobalt(0), $C_{20}H_{15}CoNO_3P$, crystallizes in the triclinic system with $a = 11·055$ (2), $b = 11·024$ (4), $c = 10·260$ (2) Å, $\alpha = 121·07$ (2), $\beta = 101·01$ (2), $\gamma = 105·14$ (2)°, $D_m = 1·39$ (5), $D_x = 1·42$ g.cm$^{-3}$, $Z = 2$; space group is $P\bar{1}$. The structure was determined from 2006 'observed' intensities collected on a G.E. XRD-5 diffractometer using Mo $K\alpha$ radiation. Nitrogen and carbon atoms in the nitrosyl and carbonyl groups are disordered. Least-squares refinement of the parameters led to a final $R$ of 3·2% when composite 'NC atoms' ($\frac{3}{4}$ C, $\frac{1}{4}$ N) were refined and also when disordered nitrogen and carbon atoms were independently refined at each location. The coordination around cobalt is slightly distorted from tetrahedral; angles between the carbonyl and nitrosyl groups average approximately 113·4° and angles between the phosphorus and the nitrosyl or carbonyl groups average approximately 105·0°. The structure consists of discrete molecular units with no indication of inter-molecular hydrogen bonding.

## Introduction

Tricarbonylnitrosylcobalt(0) and its triphenylphosphine derivatives have been of interest for some time. (Cable & Sheline, 1956; Beck & Lottes, 1965; Beck & Melnikoff, 1965). These cobalt species are isoelectronic with nickel tetracarbonyl and are postulated to have a similar molecular structure. The tetrahedral configuration of nickel tetracarbonyl was established by the elec-tron-diffraction study of Brockway & Cross (1935) and by the X-ray diffraction study of Ladell, Post & Fankuchen (1952); the tetrahedral configuration of the 'pseudo-nickel carbonyls'* $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ was established by the electron-diffraction study of

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* Name applied to the series of compounds $Ni(CO)_4$, $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $Mn(CO)(NO)_3$, and $Cr(NO)_4$ by Huber & Anderson (1931).

Brockway & Anderson (1937). To date, no structural investigations have been reported (using diffraction methods) for the triphenylphosphine derivatives of the '*pseudo*-nickel carbonyls'.

During investigations of the photochemical dimerization of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) using '*pseudo*-nickel carbonyls' and their triphenylphosphine derivatives as catalysts, a significant difference was found between the behavior of the cobalt species and nickel tetracarbonyl (Jennings & Voecks, 1970).

The coupling of the photochemical difference which suggests perhaps that these two species might not have similar molecular structures with the possibility, although remote, that the nitrosyl group might be bent led us to investigate the crystal and molecular structure of dicarbonylnitrosyltriphenylphosphinecobalt(0).
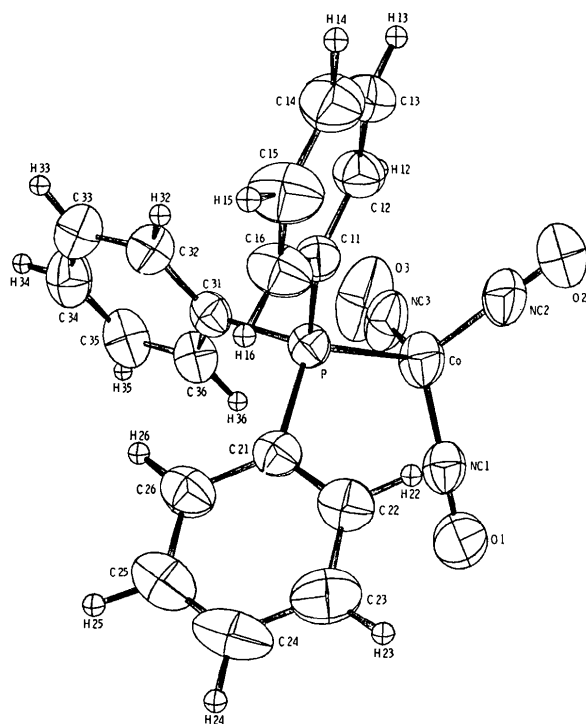


Fig. 1. Dicarbonylnitrosyltriphenylphosphinecobalt(0), illustrating the thermal ellipsoids.
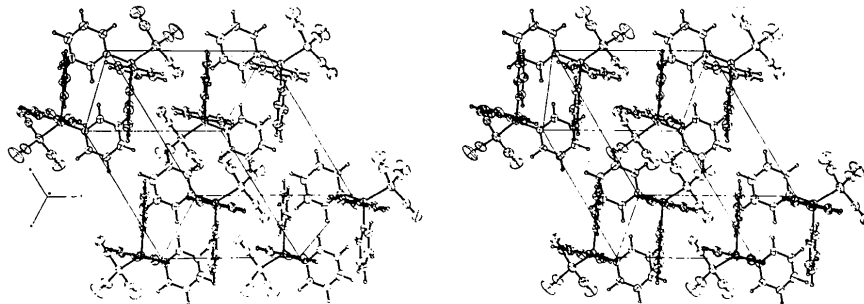
## Experimental

Crystals used in this investigation were prepared as follows: $Co(CO)_3NO$† was purified by trap-to-trap distillation on a vacuum line; under $N_2$ at 1 atm and in toluene solvent, triphenylphosphine and $Co(CO)_3NO$ were mixed in the molar ratio of 3 to 2 and heated until no further evolution of CO was observed; the toluene was evaporated and the remaining solid was dissolved in a 5:1 volume ratio of hexane and dichloromethane; the solution was placed on an alumina column and eluted with hexane; the solid from the first fraction was recrystallized from hexane, yielding the red crystalline product melting in the range 136·0–136·5 °C. It was not considered necessary to obtain an elemental analysis of the crystalline product since: (1) other reaction products (*i.e.*, the bis-triphenylphosphine derivative) are separated on the alumina column, (2) the presence of one and only one NO group is determined by the electronic configuration of cobalt(0) (and the presence of NO is verified by the infrared spectra), and (3) the compound exhibited a sharp well-defined melting point.

Preliminary photographic examination of a single crystal of dicarbonylnitrosyltriphenylphosphinecobalt(0), $C_{20}H_{15}CoNO_3P$, indicated that it is in the triclinic system. Precise parameters of the Delauney unit cell were determined on a G. E. XRD-5 diffractometer and single-crystal orienter using Mo $K\alpha$ radiation by the least-squares refinement of 30 $2\theta$ values. Crystal data are listed in Table 1.

Table 1. *Crystal data*

Dicarbonylnitrosyltriphenylphosphinecobalt(0)

$C_{20}H_{15}CoNO_3P$     F.W. 407·25     $F(000) = 416$

Triclinic, space group $P\bar{1}$

| | |
|---|---|
| $a = 11·055$ (2) Å | $\alpha = 121·07$ (2)° |
| $b = 11·024$ (4) | $\beta = 101·01$ (2) |
| $c = 10·260$ (2) | $\gamma = 105·14$ (2) |
| $V = 950·31$ Å³ | $D_m = 1·39$ (5) g.cm⁻³ |
| $Z = 2$ | $D_x = 1·42$ g.cm⁻³ |

The density, determined by flotation in a mixture of benzene and chloroform, is 1·39(5) g.cm⁻³. Several

† Purchased from Strem Chemicals, Dover, Mass.



Fig. 2. Stereo packing diagram.

small crystals were used while adjusting the composition of the mixture, as the crystals dissolve rapidly. The unique intensity data were collected by $\theta$–$2\theta$ scans using zirconium-filtered Mo $K\alpha$ radiation ($\lambda =$ 0·7107 Å) and a General Electric XRD-5 diffractometer equipped with a scintillation counter, pulse-height dis-

## Table 2. Observed and calculated structure amplitudes

Within each group are given the values of $h$, $F_o$, and $F_c$. 'Unobserved' data are indicated by double asterisks (**).

### Table 2 (cont.)



criminator, and a General Electric single-crystal orienter. The crystal was mounted with the [$\bar{1}\bar{1}3$] vector parallel to the spindle axis. Sixty-second scans (2° in 2$\theta$) were used with stationary backgrounds measured for 30 sec each at the start and finish of each scan. A chart recording of diffracted intensity vs. 2$\theta$ was monitored during data collection to insure that the reflections were centered in the scan range. Of the 2907 unique reflections examined within the range 2$\theta \le 50°$, 2006 had an intensity greater than twice the standard deviation of the intensity; the remaining 901 reflections were coded as 'unobserved' and were not included in the refinement.

Dimensions of the crystal were measured, in preparation to applying absorption corrections, using a calibrated 'Whipple disc'[†] in the alignment telescope. The crystal was well shaped, bound by the planes {010},

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[†] The 'Whipple disc' is a grid replacing the cross-hair reticle. Grid spacing of our 10 × 10 grid (Bausch and Lomb Cat. No. 31-16-13) is 0·128 mm as superimposed on the image. One grid unit near the center is further divided into a 5 × 5 grid.

{100}, {1̄10}, {01̄1}, and {1̄01}, and its dimensions in the directions of $a^*$, $b^*$ and $c$ were approximately 0·19, 0·39, and 0·56 mm. The linear absorption coefficient for Mo $K\alpha$ radiation is 11·01 cm$^{-1}$; absorption corrections, using the method of de Meulenaer & Tompa (1965), gave transmission coefficients ($I/I_o$) ranging from 0·915 to 0·851.

### Structure determination and refinement

All calculations were carried out on an XDS Sigma 7 computer.† Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for all atoms other than hydrogen; those for hydrogen were taken from Table II of Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections were applied to $F_c$ for cobalt ($\Delta f' = 0·4$, $\Delta f'' = 1·1$) and phosphorus ($\Delta f' = 0·1$, $\Delta f'' = 0·2$).

The positions of the cobalt and phosphorus atoms were determined from a three-dimensional Patterson map. The positions of the remaining nonhydrogen atoms

were determined from a three-dimensional Fourier map. The structure was refined by full-matrix least squares using the weighting scheme described by Stout & Jensen (1968),† refining the nitrogen and carbon atoms in the nitrosyl and carbonyl groups as composite 'NC atoms' consisting of ⅓ N and ⅔ C in their scattering factor curves, and refining all atoms anisotropically.

Disorder in the nitrosyl and carbonyl groups has been reported in other transition metal complexes (Enemark & Ibers, 1967, 1968) and was predicted to occur in the present complex (Ibers, 1970). Examination of the resultant bond lengths and thermal parameters of the nitrogen and carbon atoms (refined as composite 'NC atoms') in the nitrosyl and carbonyl groups could not distinguish nitrogen from the carbon atoms. Since we were unable to distinguish between nitrogen and carbon, the refinement was continued assuming disorder in the nitrogen and carbon atoms in the nitrosyl and carbonyl groups.

Positions of the phenyl hydrogen atoms were calculated assuming a C–H bond length of 1·05 Å. The structure was refined by full-matrix least squares, refining

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† F. R. Ahmed *et al.* NRC-2, *Data Reduction and Tape Generation;* NRC-8, *Fourier for Distorted and Undistorted Nets;* NRC-10, *Structure Factor Least Squares (Block Diagonal);* and NRC-12, *Scan of Interatomic Distances and Angles;* National Research Council, Ottawa, Ontario, Canada. Busing & Levy (1959), *A Crystallographic Least Squares Program for the IBM 704.* Johnson (1965), *ORTEP.* These programs were locally modified for use with the XDS Sigma 7 computer. Other programs were written locally by C. N. Caughlan, E. L. Enwall, G. D. Smith, D. L. Ward & K. D. Watenpaugh.

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† A constant of 0·032 was used to allow for instrumental instability; Stout & Jensen's equation is

$$\sigma F = \frac{1}{2}\frac{k}{\sqrt{LP}}\sqrt{\frac{N_t + N_{bg1} + N_{bg2} + (0·032\ N_{pk})^2}{N_t - N_{bg1} - N_{bg2}}}$$

where $\sigma F$, $k$, $1/\sqrt{LP}$, $N_t$, $N_{bg1}$, $N_{bg2}$, and $N_{pk}$ are the standard deviation in $F$, scale, Lorentz–polarization factor, total counts, background counts on either side of the peak, and net peak count, respectively. Weights, $w$, are $1/\sigma_F^2$.

### Table 3. *Positional and thermal parameters of the nonhydrogen atoms*

Parameters × 10⁴, e.s.d.'s in parentheses.

| | $x/a$ | $y/b$ | $z/c$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Co | 2150 (0·5) | 1737( 0·6) | 4462 (0·6) | 147 (0·8) | 218 (1·1) | 180 (1·0) | 95 (0·7) | 108 (0·7) | 119 (0·9) |
| P | 3173 (0·9) | 1072 (1·0) | 2695 (1·0) | 102 (1·1) | 132 (1·5) | 119 (1·5) | 58 (1·1) | 56 (1·1) | 80 (1·3) |
| O(1) | 684 (3) | −1137 (3) | 3954 (3) | 186 (4) | 264 (6) | 316 (7) | 115 (4) | 133 (4) | 213 (5) |
| O(2) | 291 (3) | 2809 (4) | 3468 (4) | 174 (4) | 344 (7) | 501 (10) | 159 (5) | 151 (5) | 286 (7) |
| O(3) | 4317 (3) | 4154 (4) | 7634 (4) | 181 (5) | 345 (8) | 226 (7) | 34 (5) | 71 (4) | 11 (6) |
| NC(1) | 1282 (3) | 22 (4) | 4172 (4) | 120 (4) | 193 (7) | 160 (6) | 76 (4) | 75 (4) | 109 (5) |
| NC(2) | 1030 (4) | 2381 (4) | 3846 (5) | 137 (5) | 220 (7) | 277 (9) | 92 (5) | 123 (5) | 145 (7) |
| NC(3) | 3460 (3) | 3211 (4) | 6377 (4) | 125 (5) | 201 (7) | 204 (8) | 57 (5) | 92 (5) | 63 (6) |
| C(11) | 2850 (3) | 1553 (4) | 1247 (4) | 93 (4) | 131 (6) | 131 (6) | 52 (4) | 47 (4) | 88 (5) |
| C(12) | 2823 (4) | 2980 (5) | 1798 (5) | 138 (5) | 148 (7) | 165 (6) | 69 (5) | 72 (5) | 100 (6) |
| C(13) | 2605 (4) | 3389 (5) | 743 (6) | 165 (6) | 181 (8) | 259 (10) | 96 (6) | 102 (6) | 165 (8) |
| C(14) | 2403 (4) | 2380 (6) | −870 (6) | 158 (6) | 237 (10) | 226 (10) | 87 (6) | 70 (6) | 183 (9) |
| C(15) | 2429 (4) | 962 (5) | −1447 (5) | 218 (7) | 192 (9) | 147 (8) | 87 (6) | 73 (6) | 114 (7) |
| C(16) | 2657 (4) | 558 (5) | −380 (4) | 187 (6) | 156 (7) | 145 (7) | 88 (6) | 70 (5) | 99 (6) |
| C(21) | 2700 (4) | −1022 (4) | 1338 (4) | 121 (5) | 135 (6) | 121 (6) | 63 (5) | 61 (4) | 91 (5) |
| C(22) | 1326 (4) | −2029 (5) | 500 (4) | 144 (6) | 148 (8) | 158 (7) | 68 (6) | 60 (5) | 90 (6) |
| C(23) | 904 (5) | −3624 (5) | −554 (5) | 173 (7) | 158 (8) | 185 (8) | 43 (7) | 41 (6) | 98 (7) |
| C(24) | 1846 (6) | −4217 (6) | −762 (6) | 277 (10) | 132 (9) | 188 (9) | 102 (8) | 80 (8) | 98 (8) |
| C(25) | 3206 (6) | −3251 (6) | 65 (6) | 201 (8) | 182 (9) | 212 (9) | 118 (8) | 86 (7) | 118 (8) |
| C(26) | 3631 (5) | −1658 (5) | 1111 (5) | 148 (6) | 149 (7) | 161 (7) | 76 (6) | 69 (6) | 93 (6) |
| C(31) | 5021 (3) | 1925 (4) | 3646 (4) | 108 (4) | 122 (6) | 110 (6) | 61 (4) | 56 (4) | 65 (5) |
| C(32) | 5871 (4) | 2569 (4) | 3134 (5) | 107 (5) | 166 (7) | 145 (7) | 52 (5) | 43 (5) | 95 (6) |
| C(33) | 7256 (4) | 3164 (5) | 3867 (5) | 115 (6) | 206 (8) | 202 (9) | 55 (6) | 76 (6) | 121 (7) |
| C(34) | 7821 (5) | 3131 (5) | 5154 (5) | 102 (6) | 207 (8) | 171 (9) | 59 (6) | 35 (6) | 67 (7) |
| C(35) | 7014 (5) | 2522 (5) | 5705 (5) | 146 (6) | 243 (9) | 149 (7) | 108 (6) | 62 (6) | 116 (7) |
| C(36) | 5630 (4) | 1942 (4) | 4992 (4) | 116 (5) | 189 (7) | 152 (7) | 77 (5) | 63 (5) | 106 (6) |

Expression for the anisotropic thermal parameters is of the form:
$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl).$$

the nonhydrogen atoms anisotropically and the hydrogen atoms isotropically, applying anomalous dispersion corrections to cobalt and phosphorus, and using the weighting scheme of Stout & Jensen. The final $R$ was 3·2% and the final $R_{wtd}$ was 3·5% where $R$ and $R_{wtd}$ are defined as

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|} \qquad R_{wtd} = \left[ \frac{\sum (\sqrt{w}|F_o - F_c|)^2}{\sum (\sqrt{w}|F_o|)^2} \right]^{\frac{1}{2}}$$

and the function minimized during refinement was

$$\sum \sqrt{w}(|F_o| - \frac{1}{k}|F_c|)^2.$$

The final $R$ including 'unobserved' data was 8·8%, and the final $R$ for 'unobserved' data only was 53·1%.

Table 2 lists observed and calculated values for $F$ for all 2907 reflections examined; 'unobserved' data are indicated by double asterisks (**). Positional and thermal parameters for the nonhydrogen atoms are listed in Table 3; those for the hydrogen atoms are listed in Table 4.

Table 4. *Positional and thermal parameters for hydrogen atoms*

Parameters × 10³, e.s.d'.s in parentheses.

|  | x/a | y/b | z/c | $B_{iso}(\times 1)$ |
|---|---|---|---|---|
| H(12) | 302 (3) | 367 (4) | 293 (4) | 4·6 (8) |
| H(13) | 261 (3) | 441 (4) | 117 (4) | 5·5 (9) |
| H(14) | 226 (4) | 268 (4) | −156 (5) | 7·2 (11) |
| H(15) | 239 (4) | 28 (5) | −254 (5) | 7·9 (12) |
| H(16) | 267 (3) | −46 (4) | −85 (4) | 5·0 (9) |
| H(22) | 69 (3) | −156 (4) | 66 (4) | 4·5 (8) |
| H(23) | −9 (4) | −427 (5) | −108 (5) | 7·7 (12) |
| H(24) | 158 (3) | −526 (4) | −139 (4) | 5·5 (10) |
| H(25) | 397 (4) | −356 (4) | 5 (4) | 6·4 (10) |
| H(26) | 457 (3) | −98 (4) | 162 (4) | 3·8 (8) |
| H(32) | 549 (3) | 259 (4) | 227 (4) | 4·6 (8) |
| H(33) | 776 (3) | 359 (4) | 351 (4) | 4·0 (8) |
| H(34) | 871 (4) | 354 (4) | 563 (4) | 4·9 (9) |
| H(35) | 732 (3) | 244 (4) | 659 (4) | 5·8 (9) |
| H(36) | 501 (3) | 146 (4) | 532 (4) | 4·5 (8) |

The structure was also refined with a carbon atom and a nitrogen atom at each 'NC atom' position, refining occupation factors and independent positional and thermal parameters. This refinement yielded carbon and nitrogen positions within 0·03 Å of the corresponding 'NC atom' positions, thermal parameters similar to those from the earlier refinement, and a final $R$ of 3·2% and $R_{wtd}$ of 3·5%. Parameters of the other atoms refined to within one standard deviation of their earlier values. Occupation factors were 0·31 (4) for N(1) [corresponds to atom NC(1)] and 0·22 (4) for N(2). Occupation factors for the remaining atoms are 0·46 for N(3), 0·69 for C(1), 0·78 for C(2) and 0·54 for C(3). These occupation-factor values give additional justification for the use of the composite 'NC atoms' in representing the disordered nitrogen and carbon atoms in the nitrosyl and carbonyl groups.

The final difference map is essentially flat with the density ranging from +0·27 to −0·21. Observed peaks do not fall at atomic positions within the molecule.

## The structure

The coordination about the cobalt and phosphorus is slightly distorted from tetrahedral. Average angles are: NC–Co–NC (113·5°), NC–Co–P (105·1°), C–P–C (103·2°), and Co–P–C (115·2°).

The molecule is rotated about the Co–P bond such that the carbonyl-nitrosyl groups nearly eclipse the phenyl groups; the angle that the molecule is rotated away from being fully eclipsed is 6·0° [angle NC(1)–Co–P–C(21)]. As the phenyl groups are rotated about the P–C($x$1) bonds to give a 'propeller' arrangement, the eclipsed configuration with the carbonyl-nitrosyl groups appears to give a minimum of steric interaction within the molecule. This is shown in Fig. 1, a drawing of the molecule which also illustrates the thermal ellipsoids.

One hydrogen atom of each phenyl ring is placed above atom C($x$1) of another ring to give the following short nonbonded contacts:

| C(11)–H(32) | 2·60 (4) Å |
|---|---|
| C(21)–H(16) | 2·62 (4) |
| C(31)–H(26) | 2·59 (4) |

Assuming an aromatic hydrogen van der Waals radius of 1·0 Å (Bondi, 1964) and a phenyl ring thickness of 3·2 Å, a minimum nonbonded contact of 2·6 Å would be expected. Observed distances are not significantly less than 2·6 Å, thereby giving no indication of strong hydrogen-bond interactions; short distances appear to be the result of minimizing steric interactions within the molecule as a whole.

Table 5. *Bond distances*

| | | | |
|---|---|---|---|
| Co—P | 2·224 (1) Å | C(25)–C(26) | 1·374 (8) |
| Co—O(1) | 2·868 (4) | C(26)–C(21) | 1·380 (7) |
| Co—O(2) | 2·894 (4) | C(31)–C(32) | 1·375 (6) |
| Co—O(3) | 2·858 (3) | C(32)–C(33) | 1·367 (7) |
| Co—NC(1) | 1·717 (5) | C(33)–C(34) | 1·371 (7) |
| Co—NC(2) | 1·749 (5) | C(34)–C(35) | 1·357 (8) |
| Co—NC(3) | 1·729 (4) | C(35)–C(36) | 1·365 (7) |
| O(1)—NC(1) | 1·152 (6) | C(36)–C(31) | 1·403 (6) |
| O(2)—NC(2) | 1·145 (6) | C(12)–H(12) | 0·94 (3) |
| O(3)—NC(3) | 1·130 (5) | C(13)–H(13) | 0·98 (5) |
| P——C(11) | 1·824 (4) | C(14)–H(14) | 0·93 (5) |
| P——C(21) | 1·821 (4) | C(15)–H(15) | 0·96 (4) |
| P——C(31) | 1·816 (4) | C(16)–H(16) | 0·97 (4) |
| C(11)–C(12) | 1·382 (7) | C(22)–H(22) | 0·96 (4) |
| C(12)–C(13) | 1·376 (8) | C(23)–H(23) | 0·98 (5) |
| C(13)–C(14) | 1·362 (7) | C(24)–H(24) | 0·90 (5) |
| C(14)–C(15) | 1·368 (9) | C(25)–H(25) | 0·99 (5) |
| C(15)–C(16) | 1·384 (8) | C(26)–H(26) | 0·94 (4) |
| C(16)–C(11) | 1·374 (5) | C(32)–H(32) | 0·92 (4) |
| C(21)–C(22) | 1·383 (6) | C(33)–H(33) | 0·89 (4) |
| C(22)–C(23) | 1·377 (8) | C(34)–H(34) | 0·88 (4) |
| C(23)–C(24) | 1·361 (10) | C(35)–H(35) | 0·96 (4) |
| C(24)–C(25) | 1·363 (9) | C(36)–H(36) | 0·97 (4) |

Intermolecular nonbonded contacts between oxygen and phenyl carbon atoms range as short as 3·17 Å. Assuming van der Waals radii of 1·77 Å for aromatic carbon and 1·50 Å for carbonyl oxygen (Bondi. 1964), a minimum nonbonded contact of 3·3 Å would be expected. However, angles O···H---C are far from linear; the least-acute is about 134°. This far departure from linearity, coupled with the lack of oxygen–carbon distances significantly less than 3·3 Å, indicates that there are no strong intermolecular hydrogen-bond interactions.

Least-squares planes were calculated using unit weights for each of the three phenyl rings with and without the phosphorus atom. Maximum deviations from the planes of the individual rings with and without the phosphorus are 0·005 and 0·004 Å for the ring containing C(11), 0·010 and 0·004 Å for the ring containing C(21), and 0·024 and 0·013 Å for the ring containing C(31), respectively.

Bond lengths are listed in Table 5, and bond angles are listed in Table 6. A packing diagram is shown in Fig. 2.

It is interesting to note that the 'propeller' arrange-

ment of the phenyl rings gives a helical sense to the molecule. The second molecule in the unit cell, related to the first by a center of symmetry, has the opposite helical sense. It appears from studying models that the interconversion between the two helical senses is accomplished by simultaneous rotation about the Co–P bond and about the three P–C(x1) bonds; rotation about the Co–P bond is approximately 110°.

The comparison of the M–C bond lengths with those in Co(CO)₃(NO) and other 'pseudo-nickel carbonyls' is shown in Table 7 and indicates a significant shortening of the M–NC bonds. This phenomenon also occurred in Mn(CO)₄(NO) with increasing substitution of the carbonyl groups by triphenylphosphine (Enemark & Ibers, 1967, 1968; Frenz, Enemark & Ibers, 1969).

The shortening of the metal–carbon bond lengths with increasing substitution of the carbonyl by triphenylphosphine may be explained qualitatively as follows: phosphorus (as in triphenylphosphine) is less adept at back-bonding to the transition metal than is carbon of a carbonyl group. Substitution of the carbonyl group by triphenylphosphine would cause the loss of the

Table 6. *Bond angles*

| | | | | | |
|---|---|---|---|---|---|
| P——Co——NC(1) | 104·2 (1)° | P——C(21)–C(22) | 117·8 (3)° | C(16)–C(15)–H(15) | 118· (3)° |
| P——Co——NC(2) | 106·3 (2) | P——C(21)–C(26) | 123·8 (3) | C(15)–C(16)–H(16) | 116· (2) |
| P——Co——NC(3) | 104·7 (1) | C(21)–C(22)–C(23) | 120·5 (5) | C(11)–C(16)–H(16) | 123· (2) |
| NC(1)–Co——NC(2) | 111·4 (2) | C(22)–C(23)–C(24) | 119·8 (5) | C(21)–C(22)–H(22) | 117· (2) |
| NC(1)–Co——NC(3) | 116·3 (2) | C(23)–C(24)–C(25) | 120·8 (6) | C(23)–C(22)–H(22) | 122· (2) |
| NC(2)–Co——NC(3) | 112·9 (2) | C(24)–C(25)–C(26) | 119·6 (6) | C(22)–C(23)–H(23) | 116· (3) |
| Co——NC(1)–O(1) | 179·0 (4) | C(25)–C(26)–C(21) | 120·9 (5) | C(24)–C(23)–H(23) | 124· (3) |
| Co——NC(2)–O(2) | 178·7 (4) | C(26)–C(21)–C(22) | 118·4 (4) | C(23)–C(24)–H(24) | 121· (3) |
| Co——NC(3)–O(3) | 178·8 (4) | P——C(31)–C(32) | 123·9 (3) | C(25)–C(24)–H(24) | 118· (3) |
| Co——P——C(11) | 116·5 (1) | P——C(31)–C(36) | 118·6 (3) | C(24)–C(25)–H(25) | 127· (3) |
| Co——P——C(21) | 113·9 (1) | C(31)–C(32)–C(33) | 121·6 (4) | C(26)–C(25)–H(25) | 113· (3) |
| Co——P——C(31) | 115·1 (1) | C(32)–C(33)–C(34) | 119·6 (5) | C(25)–C(26)–H(26) | 120· (2) |
| C(11)–P——C(21) | 102·9 (2) | C(33)–C(34)–C(35) | 120·4 (5) | C(21)–C(26)–H(26) | 119· (2) |
| C(11)–P——C(31) | 103·5 (2) | C(34)–C(35)–C(36) | 120·4 (5) | C(31)–C(32)–H(32) | 118· (2) |
| C(21)–P——C(31) | 103·3 (2) | C(35)–C(36)–C(31) | 120·5 (4) | C(33)–C(32)–H(32) | 120· (2) |
| P——C(11)–C(12) | 119·4 (3) | C(36)–C(31)–C(32) | 117·5 (4) | C(32)–C(33)–H(33) | 118· (2) |
| P——C(11)–C(16) | 122·4 (3) | C(11)–C(12)–H(12) | 117· (2) | C(34)–C(33)–H(33) | 122· (2) |
| C(11)–C(12)–C(13) | 120·8 (4) | C(13)–C(12)–H(12) | 122· (2) | C(33)–C(34)–H(34) | 119· (3) |
| C(12)–C(13)–C(14) | 120·2 (5) | C(12)–C(13)–H(13) | 119· (2) | C(35)–C(34)–H(34) | 121· (3) |
| C(13)–C(14)–C(15) | 120·2 (5) | C(14)–C(13)–H(13) | 121· (2) | C(34)–C(35)–H(35) | 126· (3) |
| C(14)–C(15)–C(16) | 119·5 (5) | C(13)–C(14)–H(14) | 119· (3) | C(36)–C(35)–H(35) | 114· (3) |
| C(15)–C(16)–C(11) | 121·2 (4) | C(15)–C(14)–H(14) | 121· (3) | C(35)–C(36)–H(36) | 123· (2) |
| C(16)–C(11)–C(12) | 118·2 (4) | C(14)–C(15)–H(15) | 122· (3) | C(31)–C(36)–H(36) | 116· (2) |

Table 7. *Comparison of nitrosyl and carbonyl bond lengths* (Å)

Lengths are averaged where there are two or more equivalent bonds.

| Study | M---C | C---O | M---O | M---N | N---O | M---O |
|---|---|---|---|---|---|---|
| Ni(CO)₄, electron[a] | 1·82 (2) | 1·15 (3) | 2·97 | | | |
| Ni(CO)₄, X-ray[b] | 1·84 (3) | 1·15 | 2·99 (3) | | | |
| Co(CO)₃(NO), electron[c] | 1·83 (2) | 1·14 (3) | 2·97 | 1·76 (3) | 1·10 (4) | 2·86 |
| Fe(CO)₂(NO)₂, electron[c] | 1·84 (2) | 1·15 (3) | 2·99 | 1·77 (2) | 1·12 (3) | 2·89 |
| | M---NC | NC---O | M---O | | | |
| Co(CO)₂(NO)P(Ph)₃, X-ray[d] | 1·732 (4) | 1·142 (6) | 2·873 (4) | | | |

a. Brockway & Cross (1935).
b. Ladell, Post & Fankuchen (1952).
c. Brockway & Anderson (1937).
d. Present study

back-bonding attributed to the carbonyl group and, thereby, one would expect an increase in the bond order of the remaining metal-carbon (nitrogen) bonds.

In the three canonical forms for bonding in the carbonyl group ($M-C \equiv O$, $M=C=O$, and $M \equiv C-O$), as the C–O bond order changes, the M–C bond order changes in the opposite direction; therefore, the C–O and N–O stretching frequencies may be empirical monitors of the M–C and M–N bond orders. Infrared spectra have been studied (Jennings & Voecks, 1970) to give support to this explanation:

| | $Co(CO)_3(NO)$ | $Co(CO)_2(NO)P(Ph)_3$ | $\triangle_v$ |
|---|---|---|---|
| $C-O_v(a)$ | $2100 \text{ cm}^{-1}$ | 2036 | 64 |
| $(b)$ | 2035 | 1982 | 53 |
| $N-O_v$ | 1805 | 1760 | 45 |

In each case the stretching frequencies are lowered as the carbonyl group is substituted by triphenylphosphine. This indicates a decrease in the C–O and N–O bond orders and presumably an increase in the M–C and M–N bond orders. One would then expect a lengthening of the C–O and N–O bond lengths and a shortening of the M–C and M–N bond lengths.

As in the study of the $Mn(CO)_4(NO)$ series, the $Co(CO)_3(NO)$ series shows a decrease in the M–C and M–N bond lengths (observed as a decrease in the M–NC bond lengths), and shows essentially no change in the nitrosyl or carbonyl bond lengths (observed as NC–O bond lengths).

It would be interesting to investigate the structure of $Co(CO)(NO)(P(Ph)_3)_2$, of which we have good crystals on hand, to verify the explanation and prediction of the shortening of metal–carbon and metal–nitrogen bond lengths with increasing substitution of carbonyl groups by triphenylphosphine.

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