

| | | | | |
|--------|------------|------------|-------------|----------|
| C(8) | 0.2198 (7) | 0.1688 (3) | -0.1442 (3) | 4.8 (2) |
| C(9) | 0.3593 (7) | 0.1893 (3) | -0.2012 (3) | 5.1 (2) |
| C(11) | 0.636 (2) | 0.2291 (4) | 0.0402 (6) | 16.4 (8) |
| C(12) | 0.622 (3) | 0.2978 (6) | 0.0390 (8) | 21 (1) |
| C(13) | 0.552 (4) | 0.3362 (8) | -0.034 (1) | 24 (2) |
| C(14) | 0.433 (6) | 0.379 (2) | -0.032 (2) | 42 (4) |
| C(21) | 0.769 (2) | 0.0368 (5) | 0.2507 (5) | 14.5 (7) |
| C(22) | 0.936 (3) | 0.0321 (7) | 0.307 (1) | 22 (1) |
| C(23) | 1.023 (3) | -0.043 (2) | 0.330 (2) | 29 (2) |
| C(24) | 1.171 (7) | -0.031 (2) | 0.358 (3) | 25 (2) |
| C(24') | 0.897 (7) | -0.049 (3) | 0.369 (3) | 23 (2) |

Table 2. Selected geometric parameters (Å, °)

| | | | |
|-------------|-----------|--------------|-----------|
| Ni—N | 2.103 (4) | Ni—S(1) | 2.498 (2) |
| Ni—S(2) | 2.491 (3) | P—S(1) | 1.973 (3) |
| P—S(2) | 1.981 (2) | P—O(1) | 1.581 (4) |
| P—O(2) | 1.587 (4) | N—C(1) | 1.371 (5) |
| N—C(3) | 1.315 (5) | O(1)—C(11) | 1.40 (1) |
| O(2)—C(21) | 1.43 (1) | | |
| N—Ni—N' | 180.00 | S(1)—Ni—S(2) | 81.53 (8) |
| N—Ni—S(1) | 89.9 (1) | N—Ni—S(2) | 89.5 (1) |
| S(1)—P—S(2) | 111.0 (1) | O(1)—P—O(2) | 94.9 (2) |

Symmetry code: (i) 1 - x, -y, -z.

Data collection was performed using *CAD-4 Software* (Enraf-Nonius, 1989). The ω -scan width was $(0.45 + 0.35 \tan \theta)^\circ$ and the scan speed was $1-5.46^\circ \text{ min}^{-1}$. The structure was solved by direct methods and difference syntheses, and refined with anisotropic displacement parameters for all non-H atoms except C24, which was found to be disordered. Calculations were performed on a VAX3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) program package. Molecular graphics were prepared using *ORTEPII* (Johnson, 1976).

This work was supported by a grant for a Major Project from the State Science and Technology Commission, and the National Science Foundation of China, as well as the State Key Laboratory of Tribology of Tsinghua University.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: CR1171). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Cobaltacyclopentadiene Complexes and One Cyclobutadiene Complex

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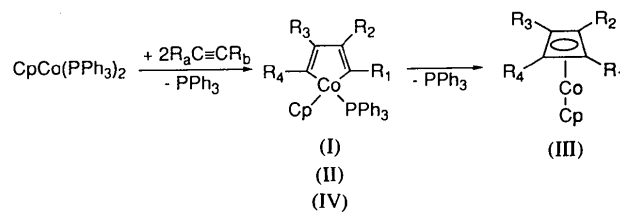
(Received 26 October 1993; accepted 9 May 1995)

Abstract

The structures of three cobalt complexes, [1,4-bis(1-propynyl)-2,3-dimethyl-1,3-butadiene-1,4-diyl](η^5 -cyclopentadienyl)(triphenylphosphine)cobalt, $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{12}\text{H}_{12})(\text{C}_{18}\text{H}_{15}\text{P})]$, (η^5 -cyclopentadienyl)[2,4-diphenyl-1,3-bis(phenylethynyl)-1,3-butadiene-1,4-diyl](triphenylphosphine)cobalt, $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{32}\text{H}_{20})(\text{C}_{18}\text{H}_{15}\text{P})]$, and $\{\eta^4$ -1,3-bis(trimethylsilyl)-2,4-bis[4'-(trimethylsilyl)ethynyl]biphenyl-4-yl]cyclobutadiene}(η^5 -cyclopentadienyl)cobalt, $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_{44}\text{H}_{52}\text{Si}_4)]$, have been determined by single-crystal X-ray diffraction.

Comment

Dialkynylcobaltacyclopentadiene complexes were obtained from the reaction of $(\text{C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ with conjugated diacetylenes. In order to identify geometric isomers, X-ray structure analyses have been carried out. The syntheses and electrochemical properties of the complexes have been published elsewhere (Shimura *et al.*, 1995).



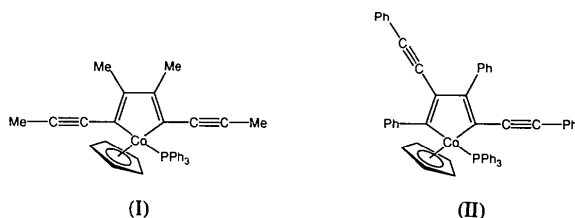
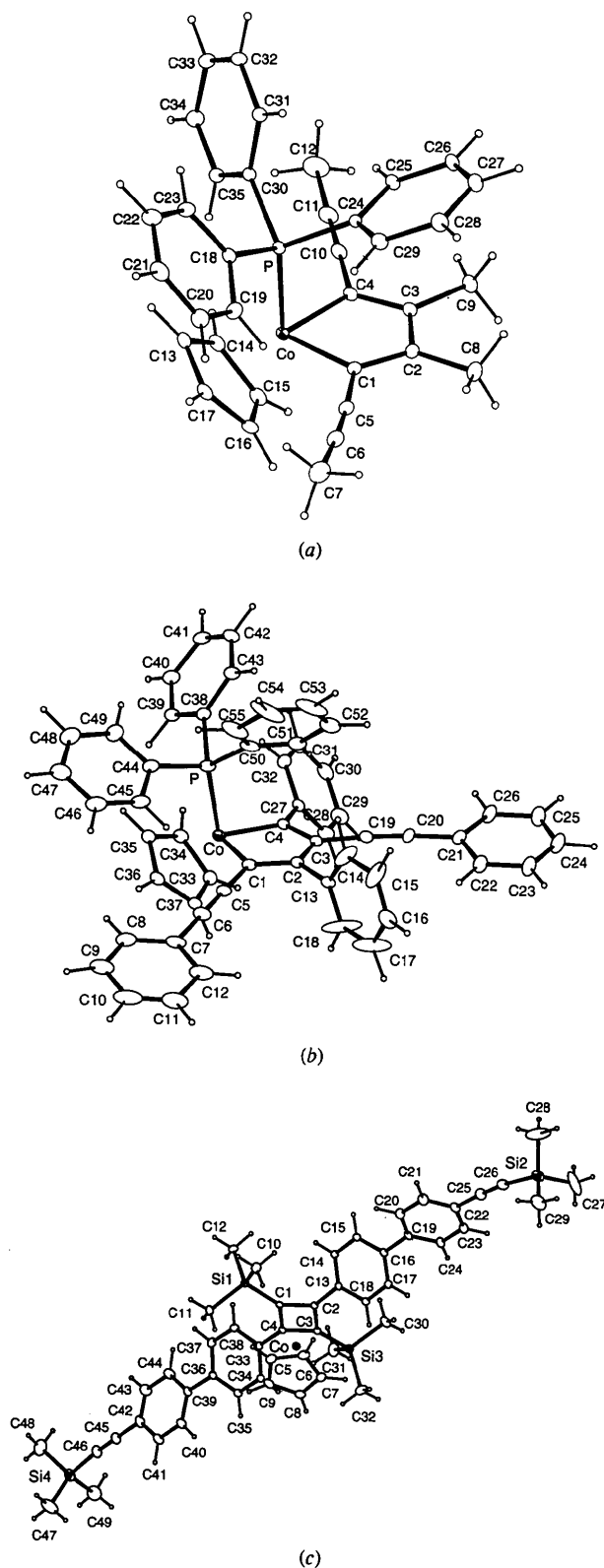
(I) $R_1 = R_4 = \text{C}\equiv\text{C-Me}$, $R_2 = R_3 = \text{Me}$

(II) $R_1 = R_3 = \text{C}\equiv\text{C-Ph}$, $R_2 = R_4 = \text{Ph}$

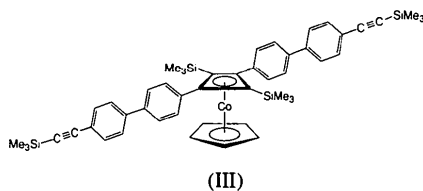
(III) $R_1 = R_3 = \text{SiMe}_3$, $R_2 = R_4 = \text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-C}\equiv\text{C-SiMe}_3$

(IV) $R_1 = R_2 = R_3 = R_4 = \text{C}_6\text{F}_5$ (Gastinger *et al.*, 1976)

Complex (I), [1,4-bis(1-propynyl)-2,3-dimethyl-1,3-butadiene-1,4-diyl](η^5 -cyclopentadienyl)(triphenylphosphine)cobalt, has chemical mirror symmetry through the Co—P axis and the midpoint of C2—C3. The two $\text{—C}\equiv\text{C—Me}$ groups are bonded to C1 and C4 of the metallacycle.



In (II), (η^5 -cyclopentadienyl)[2,4-diphenyl-1,3-bis(phenylethynyl)-1,3-butadiene-1,4-diyl](triphenylphosphine)cobalt, the two $\text{—C}\equiv\text{C—Ph}$ groups are bonded to C1 and C3 of the metallacycle. The two phenyl groups attached directly to the metallacycle form dihedral angles with the metallacyclic plane of $84.7(3)^\circ$ (around the C2—C13 bond) and $58.1(3)^\circ$ (around the C4—C27 bond). In the related complex, [Co(C₅H₅){C₄(C₆F₅)₄}(C₁₈H₁₅P)], (IV), the pentafluorophenyl groups and the metallacyclic plane are nearly perpendicular to each other (Gastinger, Rausch, Sullivan & Palenik, 1976). This may be the result of intramolecular steric repulsions between the phenyl groups.



Complex (III), { η^4 -1,3-bis(trimethylsilyl)-2,4-bis[4'-(trimethylsilylethynyl)biphenyl-4-yl]cyclobutadiene}(η^5 -cyclopentadienyl)cobalt, has chemical mirror symmetry through atoms Co, C1 and C3. The Co atom is sandwiched between the cyclobutadiene and cyclopentadiene rings, which are nearly parallel to each other having a dihedral angle of $1.1(3)^\circ$. The dihedral angles between the cyclobutadiene ring and phenyl rings A (C13—C18) and C (C33—C38) attached to it are $37.3(3)^\circ$ and $41.6(3)^\circ$, respectively. The dihedral angles of the biphenyl moieties A—B (C19—C24) and C—D (C39—C44) are $39.8(3)^\circ$ and $23.7(3)^\circ$, respectively. As nearly all the C—C bond distances of the cyclobutadiene unit are the same, delocalization of the double bonds is indicated.

Experimental

Crystals of (I) and (II) were grown from a benzene–hexane mixture. Compound (III) was recrystallized from an acetonitrile–benzene mixture.

Compound (I)

Crystal data

[Co(C₅H₅)(C₁₂H₁₂)-(C₁₈H₁₅P)]

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Fig. 1. ORTEP drawings (Johnson, 1965) of the molecular structures of (a) compound (I), (b) compound (II) and (c) compound (III), with displacement ellipsoids scaled to the 10% probability level.

$M_r = 542.55$
 Monoclinic
 $P2_1/n$
 $a = 17.411(2) \text{ \AA}$
 $b = 15.756(2) \text{ \AA}$
 $c = 10.593(1) \text{ \AA}$
 $\beta = 107.19(1)^\circ$
 $V = 2776.1(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.30 \text{ Mg m}^{-3}$

Cell parameters from 24 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 0.69 \text{ mm}^{-1}$
 $T = 300 \text{ K}$
 Prism
 $0.60 \times 0.30 \times 0.30 \text{ mm}$
 Dark brown

| | | | | |
|-----|------------|-------------|------------|-----|
| C24 | 0.3053 (1) | -0.0428 (2) | 0.1683 (2) | 2.5 |
| C25 | 0.3343 (2) | -0.0314 (2) | 0.3042 (2) | 3.1 |
| C26 | 0.4097 (2) | -0.0610 (2) | 0.3752 (3) | 3.8 |
| C27 | 0.4571 (2) | -0.1007 (2) | 0.3104 (3) | 4.4 |
| C28 | 0.4301 (2) | -0.1108 (2) | 0.1754 (3) | 4.8 |
| C29 | 0.3542 (2) | -0.0818 (2) | 0.1043 (3) | 4.0 |
| C30 | 0.1488 (1) | -0.0257 (2) | 0.1930 (2) | 2.7 |
| C31 | 0.1604 (2) | -0.1042 (2) | 0.2593 (2) | 3.1 |
| C32 | 0.1184 (2) | -0.1245 (2) | 0.3473 (2) | 3.6 |
| C33 | 0.0635 (2) | -0.0677 (2) | 0.3700 (3) | 4.1 |
| C34 | 0.0502 (2) | 0.0092 (2) | 0.3046 (3) | 4.0 |
| C35 | 0.0933 (2) | 0.0302 (2) | 0.2166 (2) | 3.3 |

Data collection

Rigaku AFC-5 four-circle diffractometer
 $\theta/2\theta$ scans
 Absorption correction: by integration from crystal shape
 $T_{\min} = 0.789$, $T_{\max} = 0.849$
 6711 measured reflections
 6376 independent reflections

4337 observed reflections
 $[|F_o| > 3\sigma(|F_o|)]$
 $R_{\text{int}} = 0.013$
 $\theta_{\max} = 27.5^\circ$
 $h = -22 \rightarrow 22$
 $k = 0 \rightarrow 20$
 $l = 0 \rightarrow 13$
 5 standard reflections monitored every 100 reflections
 intensity decay: 1.8%

Refinement

Refinement on F
 $R = 0.036$
 $wR = 0.041$
 $S = 1.56$
 4337 reflections
 333 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(|F_o|) + (0.015|F_o|)^2]$
 $(\Delta/\sigma)_{\max} = 0.20$
 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)

| | x | y | z | B_{eq} |
|-----|-------------|-------------|-------------|-----------------|
| Co | 0.20858 (2) | 0.13422 (2) | 0.02105 (3) | 2.5 |
| P | 0.20701 (4) | 0.00186 (4) | 0.07930 (6) | 2.4 |
| C1 | 0.3155 (2) | 0.1219 (2) | -0.0029 (2) | 3.0 |
| C2 | 0.3776 (2) | 0.1386 (2) | 0.1073 (3) | 3.2 |
| C3 | 0.3531 (2) | 0.1603 (2) | 0.2218 (3) | 3.0 |
| C4 | 0.2722 (2) | 0.1605 (2) | 0.2020 (2) | 2.7 |
| C5 | 0.3268 (2) | 0.0972 (2) | -0.1257 (3) | 3.5 |
| C6 | 0.3312 (2) | 0.0740 (2) | -0.2298 (3) | 4.4 |
| C7 | 0.3332 (2) | 0.0378 (3) | -0.3569 (3) | 6.7 |
| C8 | 0.4651 (2) | 0.1324 (2) | 0.1129 (3) | 5.1 |
| C9 | 0.4143 (2) | 0.1773 (2) | 0.3539 (3) | 4.1 |
| C10 | 0.2372 (2) | 0.1775 (2) | 0.3046 (2) | 3.3 |
| C11 | 0.2070 (2) | 0.1886 (2) | 0.3897 (3) | 4.6 |
| C12 | 0.1706 (3) | 0.1978 (3) | 0.4980 (4) | 7.3 |
| C13 | 0.0847 (2) | 0.1440 (2) | -0.0769 (3) | 3.8 |
| C14 | 0.1089 (2) | 0.2109 (2) | 0.0147 (3) | 3.9 |
| C15 | 0.1683 (2) | 0.2580 (2) | -0.0218 (3) | 4.2 |
| C16 | 0.1796 (2) | 0.2201 (2) | -0.1358 (3) | 4.0 |
| C17 | 0.1285 (2) | 0.1496 (2) | -0.1699 (2) | 3.8 |
| C18 | 0.1672 (2) | -0.0722 (2) | -0.0596 (2) | 2.7 |
| C19 | 0.1918 (2) | -0.0637 (2) | -0.1721 (3) | 4.0 |
| C20 | 0.1666 (2) | -0.1191 (2) | -0.2773 (3) | 4.6 |
| C21 | 0.1157 (2) | -0.1845 (2) | -0.2729 (3) | 4.6 |
| C22 | 0.0878 (2) | -0.1920 (2) | -0.1648 (3) | 5.2 |
| C23 | 0.1133 (2) | -0.1368 (2) | -0.0584 (3) | 4.0 |

$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

Table 2. Selected geometric parameters (\AA , $^\circ$) for (I)

| | | | |
|----------|-----------|----------|-----------|
| Co—P | 2.177 (1) | Co—C13 | 2.104 (2) |
| Co—C1 | 1.962 (3) | Co—C14 | 2.100 (3) |
| Co—C4 | 1.954 (2) | Co—C15 | 2.077 (3) |
| C1—C2 | 1.362 (3) | Co—C16 | 2.086 (3) |
| C2—C3 | 1.442 (4) | Co—C17 | 2.104 (2) |
| C3—C4 | 1.361 (4) | | |
| P—Co—C1 | 92.0 (1) | C1—C2—C3 | 114.1 (2) |
| P—Co—C4 | 88.6 (1) | C2—C3—C4 | 114.9 (2) |
| C1—Co—C4 | 82.1 (1) | Co—C4—C3 | 114.3 (2) |
| Co—C1—C2 | 114.5 (2) | | |

Compound (II)**Crystal data**

[Co(C₅H₅)(C₃₂H₂₀)-
 (C₁₈H₁₅P)]
 $M_r = 790.78$
 Monoclinic
 $P2_1/c$
 $a = 15.310(2) \text{ \AA}$
 $b = 22.997(3) \text{ \AA}$
 $c = 11.928(1) \text{ \AA}$
 $\beta = 103.35(1)^\circ$
 $V = 4086.2(8) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.29 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 33 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 0.49 \text{ mm}^{-1}$
 $T = 297 \text{ K}$
 Prism
 $0.50 \times 0.25 \times 0.20 \text{ mm}$
 Deep red

Data collection

Rigaku AFC-5 four-circle diffractometer
 $\theta/2\theta$ scans
 Absorption correction: by integration from crystal shape
 $T_{\min} = 0.851$, $T_{\max} = 0.889$
 7762 measured reflections
 7316 independent reflections

3548 observed reflections
 $[|F_o| > 3\sigma(|F_o|)]$
 $R_{\text{int}} = 0.018$
 $\theta_{\max} = 25^\circ$
 $h = -16 \rightarrow 16$
 $k = 0 \rightarrow 21$
 $l = 0 \rightarrow 14$
 5 standard reflections monitored every 100 reflections
 intensity decay: 2.0%

Refinement

Refinement on F
 $R = 0.065$
 $wR = 0.059$
 $S = 1.82$
 3548 reflections
 513 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(|F_o|) + (0.015|F_o|)^2]$
 $(\Delta/\sigma)_{\max} = 0.20$
 $\Delta\rho_{\max} = 0.85 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.93 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | B _{eq} |
|-----|-------------|-------------|-------------|-----------------|
| Co | 0.16056 (5) | 0.07592 (4) | 0.49433 (7) | 3.7 |
| P | 0.2821 (1) | 0.13022 (9) | 0.5413 (2) | 4.6 |
| C1 | 0.1444 (4) | 0.0712 (4) | 0.6530 (5) | 4.3 |
| C2 | 0.1810 (4) | 0.0227 (3) | 0.7104 (5) | 4.2 |
| C3 | 0.2216 (4) | -0.0170 (3) | 0.6428 (5) | 4.2 |
| C4 | 0.2201 (4) | 0.0018 (3) | 0.5331 (5) | 3.7 |
| C5 | 0.0914 (4) | 0.1113 (3) | 0.6991 (5) | 4.5 |
| C6 | 0.0432 (5) | 0.1439 (4) | 0.7334 (6) | 5.8 |
| C7 | -0.0148 (5) | 0.1832 (5) | 0.7766 (6) | 6.3 |
| C8 | -0.0438 (6) | 0.2357 (5) | 0.7208 (8) | 7.6 |
| C9 | -0.0997 (6) | 0.2724 (4) | 0.765 (1) | 9.5 |
| C10 | -0.1285 (8) | 0.2548 (7) | 0.861 (1) | 11.3 |
| C11 | -0.1024 (9) | 0.2053 (7) | 0.915 (1) | 10.5 |
| C12 | -0.0439 (5) | 0.1664 (5) | 0.8740 (8) | 8.8 |
| C13 | 0.1786 (4) | 0.0098 (4) | 0.8340 (6) | 5.5 |
| C14 | 0.2430 (7) | 0.0203 (4) | 0.9200 (7) | 10.1 |
| C15 | 0.2404 (9) | 0.0056 (4) | 1.0318 (8) | 10.8 |
| C16 | 0.1731 (7) | -0.0180 (5) | 1.0585 (6) | 9.0 |
| C17 | 0.1090 (7) | -0.031 (1) | 0.973 (1) | 30 |
| C18 | 0.1123 (7) | -0.017 (1) | 0.8583 (9) | 30 |
| C19 | 0.2619 (4) | -0.0693 (4) | 0.6948 (6) | 4.5 |
| C20 | 0.2930 (5) | -0.1112 (3) | 0.7490 (6) | 4.7 |
| C21 | 0.3259 (5) | -0.1602 (3) | 0.8213 (6) | 4.9 |
| C22 | 0.3025 (5) | -0.1663 (4) | 0.9276 (7) | 6.2 |
| C23 | 0.3328 (6) | -0.2134 (4) | 0.9963 (7) | 7.0 |
| C24 | 0.3845 (7) | -0.2554 (4) | 0.9624 (8) | 7.7 |
| C25 | 0.4092 (6) | -0.2501 (4) | 0.8589 (8) | 7.2 |
| C26 | 0.3786 (6) | -0.2035 (4) | 0.7875 (6) | 5.8 |
| C27 | 0.2511 (4) | -0.0373 (3) | 0.4507 (5) | 3.8 |
| C28 | 0.2153 (5) | -0.0924 (4) | 0.4276 (7) | 5.9 |
| C29 | 0.2424 (5) | -0.1287 (4) | 0.3498 (8) | 6.7 |
| C30 | 0.3071 (6) | -0.1105 (4) | 0.2935 (7) | 6.3 |
| C31 | 0.3430 (5) | -0.0569 (4) | 0.3155 (7) | 6.2 |
| C32 | 0.3145 (5) | -0.0199 (3) | 0.3918 (6) | 5.4 |
| C33 | 0.0667 (4) | 0.0341 (3) | 0.3637 (6) | 4.8 |
| C34 | 0.1174 (4) | 0.0732 (4) | 0.3122 (5) | 4.7 |
| C35 | 0.1042 (4) | 0.1301 (4) | 0.3531 (6) | 4.7 |
| C36 | 0.0447 (4) | 0.1258 (4) | 0.4270 (6) | 4.8 |
| C37 | 0.0220 (4) | 0.0672 (4) | 0.4340 (5) | 4.4 |
| C38 | 0.3599 (4) | 0.1248 (3) | 0.4451 (6) | 4.3 |
| C39 | 0.3275 (4) | 0.1325 (3) | 0.3276 (6) | 5.4 |
| C40 | 0.3826 (5) | 0.1235 (4) | 0.2511 (6) | 6.0 |
| C41 | 0.4717 (5) | 0.1075 (4) | 0.2932 (7) | 5.8 |
| C42 | 0.5050 (4) | 0.1023 (3) | 0.4088 (6) | 5.8 |
| C43 | 0.4500 (4) | 0.1115 (3) | 0.4854 (6) | 5.2 |
| C44 | 0.2511 (4) | 0.2068 (3) | 0.5366 (6) | 4.9 |
| C45 | 0.1895 (5) | 0.2267 (4) | 0.5967 (7) | 6.5 |
| C46 | 0.1610 (6) | 0.2844 (5) | 0.5897 (8) | 7.3 |
| C47 | 0.1903 (6) | 0.3230 (4) | 0.5187 (8) | 8.1 |
| C48 | 0.2524 (6) | 0.3049 (4) | 0.4592 (8) | 8.2 |
| C49 | 0.2828 (5) | 0.2477 (4) | 0.4684 (8) | 7.0 |
| C50 | 0.3584 (4) | 0.1216 (5) | 0.6838 (6) | 6.2 |
| C51 | 0.3927 (5) | 0.0668 (5) | 0.7175 (7) | 7.3 |
| C52 | 0.4540 (6) | 0.0591 (6) | 0.8239 (9) | 9.9 |
| C53 | 0.4816 (8) | 0.111 (1) | 0.889 (1) | 14.6 |
| C54 | 0.4474 (8) | 0.1613 (9) | 0.858 (1) | 15.8 |
| C55 | 0.3862 (5) | 0.1685 (5) | 0.7524 (8) | 9.7 |

Table 4. Selected geometric parameters (Å, °) for (II)

| | | | |
|----------|-----------|----------|-----------|
| Co—P | 2.204 (2) | Co—C33 | 2.094 (6) |
| Co—C1 | 1.967 (6) | Co—C34 | 2.121 (6) |
| Co—C4 | 1.938 (6) | Co—C35 | 2.112 (7) |
| C1—C2 | 1.36 (1) | Co—C36 | 2.109 (7) |
| C2—C3 | 1.45 (1) | Co—C37 | 2.086 (6) |
| C3—C4 | 1.373 (9) | | |
| P—Co—C1 | 94.2 (2) | C1—C2—C3 | 114.6 (6) |
| P—Co—C4 | 96.6 (2) | C2—C3—C4 | 114.6 (6) |
| C1—Co—C4 | 83.0 (3) | Co—C4—C3 | 114.1 (5) |
| Co—C1—C2 | 113.6 (5) | | |

Compound (III)

Crystal data

[Co(C₅H₅)(C₄₄H₅₂Si₄)]M_r = 817.27

Monoclinic

P2₁/c

a = 16.459 (4) Å

b = 28.668 (4) Å

c = 10.269 (3) Å

β = 100.54 (2)°

V = 4764 (2) Å³

Z = 4

D_x = 1.14 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 24

reflections

θ = 10–15°

μ = 0.49 mm⁻¹

T = 300 K

Plate

0.60 × 0.50 × 0.10 mm

Yellow

Data collection

Rigaku AFC-5 four-circle

diffractometer

θ/2θ scans

Absorption correction:

by integration from crystal

shape

T_{min} = 0.780, T_{max} =

0.951

11 541 measured reflections

10 938 independent

reflections

5568 observed reflections

[|F_o| > 3σ(|F_o|)]R_{int} = 0.033θ_{max} = 27.5°

h = -21 → 21

k = 0 → 37

l = 0 → 13

5 standard reflections

monitored every 100

reflections

intensity decay: 1.2%

Refinement

Refinement on F

R = 0.060

wR = 0.083

S = 2.64

5568 reflections

486 parameters

H-atom parameters not

refined

w = 1/[σ²(|F_o|)
+ (0.015|F_o|)²](Δ/σ)_{max} = 0.15Δρ_{max} = 0.55 e Å⁻³Δρ_{min} = -0.43 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV)

Table 5. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | B _{eq} |
|-----|--------------|--------------|-------------|-----------------|
| Co | -0.51652 (4) | 0.16041 (2) | 0.00968 (6) | 3.0 |
| Si1 | -0.54941 (9) | 0.09019 (5) | 0.2587 (1) | 3.3 |
| Si2 | -1.0695 (1) | -0.08178 (8) | -0.9543 (2) | 7.7 |
| Si3 | -0.3584 (1) | 0.12200 (6) | -0.1581 (2) | 3.8 |
| Si4 | 0.1575 (1) | 0.31713 (8) | 0.9834 (2) | 6.4 |
| C1 | -0.4960 (3) | 0.1019 (2) | 0.1172 (4) | 2.6 |
| C2 | -0.5077 (3) | 0.0934 (2) | -0.0258 (4) | 2.7 |
| C3 | -0.4308 (3) | 0.1179 (2) | -0.0376 (4) | 2.9 |
| C4 | -0.4193 (3) | 0.1263 (2) | 0.1054 (4) | 2.6 |
| C5 | -0.6045 (5) | 0.2011 (2) | 0.0727 (7) | 5.6 |
| C6 | -0.6311 (4) | 0.1892 (2) | -0.0609 (7) | 5.3 |
| C7 | -0.5731 (4) | 0.2066 (2) | -0.1334 (6) | 5.0 |
| C8 | -0.5106 (4) | 0.2290 (2) | -0.0456 (6) | 5.1 |
| C9 | -0.5301 (5) | 0.2265 (2) | 0.0807 (7) | 5.7 |
| C10 | -0.6622 (4) | 0.0813 (2) | 0.1960 (6) | 5.1 |
| C11 | -0.5314 (4) | 0.1391 (2) | 0.3807 (5) | 4.7 |
| C12 | -0.5065 (4) | 0.0364 (2) | 0.3469 (5) | 4.5 |
| C13 | -0.5702 (3) | 0.0676 (2) | -0.1222 (4) | 2.8 |
| C14 | -0.6065 (3) | 0.0268 (2) | -0.0888 (5) | 3.3 |
| C15 | -0.6676 (3) | 0.0044 (2) | -0.1796 (5) | 3.6 |
| C16 | -0.6924 (3) | 0.0218 (2) | -0.3070 (5) | 3.2 |

| | | | | |
|-----|-------------|-------------|-------------|------|
| C17 | -0.6538 (3) | 0.0617 (2) | -0.3416 (5) | 3.6 |
| C18 | -0.5941 (3) | 0.0844 (2) | -0.2508 (5) | 3.6 |
| C19 | -0.7577 (3) | -0.0009 (2) | -0.4079 (5) | 3.5 |
| C20 | -0.8288 (4) | -0.0190 (2) | -0.3758 (6) | 5.6 |
| C21 | -0.8912 (4) | -0.0378 (3) | -0.4734 (7) | 6.5 |
| C22 | -0.8819 (4) | -0.0378 (2) | -0.6047 (6) | 5.0 |
| C23 | -0.8100 (4) | -0.0210 (2) | -0.6356 (6) | 5.0 |
| C24 | -0.7485 (4) | -0.0024 (2) | -0.5382 (5) | 4.6 |
| C25 | -0.9455 (4) | -0.0559 (3) | -0.7104 (7) | 6.2 |
| C26 | -0.9948 (4) | -0.0691 (2) | -0.8038 (7) | 6.7 |
| C27 | -1.0126 (8) | -0.0910 (6) | -1.088 (1) | 19.3 |
| C28 | -1.130 (1) | -0.1325 (5) | -0.936 (1) | 26.4 |
| C29 | -1.1349 (5) | -0.0319 (4) | -0.999 (1) | 10.8 |
| C30 | -0.3836 (4) | 0.0757 (2) | -0.2861 (6) | 6.3 |
| C31 | -0.2516 (4) | 0.1119 (3) | -0.0672 (7) | 7.3 |
| C32 | -0.3634 (5) | 0.1797 (3) | -0.2434 (8) | 7.7 |
| C33 | -0.3521 (3) | 0.1462 (2) | 0.2043 (4) | 3.0 |
| C34 | -0.3124 (3) | 0.1872 (2) | 0.1808 (5) | 3.8 |
| C35 | -0.2502 (3) | 0.2064 (2) | 0.2756 (5) | 4.0 |
| C36 | -0.2258 (3) | 0.1848 (2) | 0.3977 (5) | 3.4 |
| C37 | -0.2635 (3) | 0.1431 (2) | 0.4203 (5) | 4.2 |
| C38 | -0.3257 (3) | 0.1242 (2) | 0.3245 (5) | 3.6 |
| C39 | -0.1616 (3) | 0.2065 (2) | 0.5016 (5) | 3.8 |
| C40 | -0.1465 (4) | 0.2536 (2) | 0.5018 (6) | 5.2 |
| C41 | -0.0877 (4) | 0.2746 (2) | 0.5969 (7) | 5.9 |
| C42 | -0.0417 (4) | 0.2478 (3) | 0.6965 (6) | 5.4 |
| C43 | -0.0568 (4) | 0.2015 (3) | 0.6976 (7) | 7.0 |
| C44 | -0.1160 (4) | 0.1797 (2) | 0.6014 (6) | 6.3 |
| C45 | 0.0206 (4) | 0.2701 (2) | 0.7952 (6) | 5.6 |
| C46 | 0.0735 (4) | 0.2876 (3) | 0.8732 (6) | 6.3 |
| C47 | 0.1206 (6) | 0.3756 (4) | 1.024 (1) | 12.4 |
| C48 | 0.1894 (6) | 0.2812 (4) | 1.1303 (8) | 11.1 |
| C49 | 0.2447 (6) | 0.3223 (4) | 0.896 (1) | 12.0 |

Table 6. Selected geometric parameters (\AA , $^\circ$) for (III)

| | | | |
|----------|-----------|----------|-----------|
| Co—C1 | 2.002 (4) | Co—C8 | 2.052 (6) |
| Co—C2 | 1.967 (5) | Co—C9 | 2.057 (7) |
| Co—C3 | 1.990 (5) | C1—C2 | 1.466 (6) |
| Co—C4 | 1.976 (4) | C1—C4 | 1.468 (7) |
| Co—C5 | 2.054 (8) | C2—C3 | 1.473 (7) |
| Co—C6 | 2.065 (6) | C3—C4 | 1.466 (6) |
| Co—C7 | 2.068 (6) | | |
| C2—C1—C4 | 87.4 (4) | C2—C3—C4 | 87.2 (4) |
| C1—C2—C3 | 92.5 (4) | C1—C4—C3 | 92.8 (4) |

All three structures were solved using the Patterson function with *SHELXS86* software (Sheldrick, 1985). All the H atoms were calculated. In (II), B_{eq} values for the C atoms in one of the phenyl groups are abnormally large, suggesting rotational disorder. In (III), B_{eq} values for the terminal trimethylsilyl C atoms ($10.8\text{--}26.4 \text{\AA}^2$) are abnormally large, again suggesting disorder. Refinements were carried out using *CRYSTAN-GM* software (MAC Science, 1992) on a SUN SPARC2 workstation. Molecular graphics were obtained using *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Ni(Mes)[N(Ph)C(O)N(H)CMe₃]- (PMe₃)₂

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Abstract

The title compound, *trans*-(3-*tert*-butyl-1-phenylureido)-(2,4,6-trimethylphenyl)bis(trimethylphosphine)nickel(II), [Ni(C₉H₁₁)(C₁₁H₁₅N₂O)(C₃H₉P)₂], has been synthesized and its crystal structure determined as part of our continuing investigation into the reactivity and stability of the late-transition-metal amide complexes. The Ni atom has square-planar coordination geometry; two *trans* sites are occupied by PMe₃ ligands. The geometry around the amide N atom is planar due to the interaction of its lone pair with the carbonyl π system. A relatively long Ni—N bond, 1.978 (6) \AA , is interpreted as arising from a lack of significant π interaction between the amide N atom and the Ni metal centre.

Comment

Recently, the chemistry of late-transition-metal amide complexes (Groups 8–10) has been studied extensively (Bryndza & Tam, 1988; Roundhill, 1992; Boncella & Villanueva, 1994). This interest in transition-metal amide complexes arises from their potential to facilitate C—N bond formation between amine derivatives and unsaturated organic compounds. This chemistry has been slow to develop, mainly because the inability of the electronically saturated metal centre to accommodate π donation from the lone-pair electrons of the amide N atom results in a weak metal–nitrogen bond (Lappert, Power, Sanger & Srivasastrava, 1980). With newer methods for the synthesis of metal amide complexes, the chemistry of these compounds can be explored. We report the structure of the product, (I), of the reaction between a late-transition-metal amide complex and ^tBuNCO. The structure reveals that the ^tBuNCO has inserted into the N—H bond.