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Novel stable five-coordinate diorgano cobalt(III) complexes: Formation, structure, and reaction with carbon monoxide

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Abstract

A series of new five-coordinate acyl vinyl cobalt(III) complexes $Co\{\eta^1\text{-}C(C{\equiv}CPh){=}CHPh\}[C(O){-}C{=}C{-}O]\ L_2(L = PMe_3)$ (**6**–**10**) were prepared via formal insertion of diphenylbutadiyne into Co–H function of *mer*-octahedral hydrido-acyl(phenolato)-cobalt(III) complexes. The complexes are diamagnetic. One square pyramidal structure of complex **6** was confirmed by X-ray diffraction analysis. These complexes are stable in solid state. In solution, six-coordinate acyl vinyl carbonyl cobalt(III) complex **11** is approved through the reaction of complex **7** with CO and the structure of complex **11** was determined by X-ray method.

Keywords: Five-coordinate; Cobalt complex; Trimethylphosphine; Diphenylbutadiyne

1. Introduction

Transition metal hydride complexes react with diyne to provide unsaturated σ-(alkynyl)vinyl derivatives by mono-insertion of the alkyne into the M–H bond accompanying one ligand leaving [1–3]. Presently, such reactions mainly center on ruthenium complexes. For example, a ruthenium hydride complex $RuClH(CO)(PPh_3)_3$ reacts with disubstituted butadiyne $RC{\equiv}CC{\equiv}CR$ ($R = SiMe_3$, Ph, ${}^tBu$) at room temperature, giving the five-coordinatively unsaturated complexes $Ru\{\eta^1\text{-}C(C{\equiv}CR){=}CHR\}Cl(CO)(PPh_3)_2$. The highly unsaturated vinyl ligand may also coordinate as three-electron donor becoming η^3-butadienyl ligand [3].

Five-coordinate cobalt(III) complexes are not saturated coordination compounds and have significance for catalytic chemistry due to potential application as catalyst. Some examples of five-coordinate alkyl cobalt(III) macrocycle compounds are known. Most of them were synthesized as model compounds for vitamin B_{12} [4] as well as for cobalamins [5]. But so far few of five-coordinate cobalt(III) complexes have been structurally characterized [4,6].

We have recently reported some insertion reactions of trimethylphosphine-supported hydrido(acyl)enolatocobalt(III) complexes with phenylethine, trimethylsilylethine, bis(trimethylsilyl)butadiyne [7] and propynoic acid ethyl ester [8]. Products of these reactions are five-coordinate cobalt(III) complexes. One square pyramid structure was confirmed by X-ray diffraction analysis [8].

In order to study the regioselectivity of insertion reaction with different alkynes, in this paper we present some new insertion reactions of 2-acyl enolato and phenolato hydrido cobalt(III) complexes with diphenylbutadiyne.

2. Experimental

2.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. The solvents were dried by known procedures and used freshly distilled. Melting points/decomposition temperatures: sealed capillaries, uncorrected values. Literature methods were

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applied in the preparation of complexes **1**–**5** [9]. Diphenylbutadiyne was obtained by the literature method [10]. The other chemicals were used as purchased. IR: Nujol mulls between KBr discs, Bruker spectrophotometer type VECTOR 22. ^{1}H, ^{13}C and ^{31}P NMR spectra (400, 100 and 162 MHz, respectively) were recorded with a Brucker AV 400 MHz spectrometer. ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling. C, H analyses were carried out in a German ELEMENTAR Vario ELIII analyzer. Single-crystal structures were determined with Bruker AXS P4 diffractometer.

2.2. Procedures

*2.2.1. Preparation of (1-carbonyl-2-oxo-cyclohexene-diyl)-[(Z)-1-phenylethinyl-2-phenylethenyl]-trans-bis(trimethylphosphine)cobalt(III) (**6**)*

Diphenylbutadiyne (500 mg, 2.48 mmol) was added to a stirred solution of *mer*-hydrido-(1-carbonyl-2-oxo-cyclohexene-diyl)tris(trimethylphosphine)cobalt(III) (**1**) (1000 mg, 2.43 mmol) in 60 ml of pentane at room temperature. The mixture became red brown from orange yellow within 5 min. After stirring for 15 h, the solution was filtered and the solid residue was extracted with ether to crystallize at 0 °C. Red brown sheet crystals were obtained. Upon cooling to −27 °C, a second fraction of crystal **6** was collected. Yield: 600 mg (45%); m.p. 140–142 °C (dec.). *Anal.* Calc. for $C_{29}H_{37}CoO_2P_2$ (538.49 g/mol): C, 64.68; H, 6.93. Found: C, 64.60; H, 6.95%. IR (Nujol): $v = 2141$ (C≡C); 1660, 1627 (C=O); 1592, 1544, 1508 (C=C) cm^{-1}. ^{1}H NMR (d_8-THF, 300 K): $\delta = 1.04$ (t′, $|^{2}J(\mathrm{PH}) + {}^{4}J(\mathrm{PH})| = 7.6$ Hz, 18H, PCH_3), 1.36 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 2.08 (s, 4H, CH_2), 6.68 (t, $^{4}J(\mathrm{PH}) = 3.8$ Hz, 1H, C=CH), 6.68–7.56 (m, 10H, CH) ppm. ^{13}C NMR (d_8-THF, 300 K): $\delta = 9.9$ (t′, $|^{1}J(\mathrm{PC}) + {}^{3}J(\mathrm{PC})| = 25.0$ Hz, PCH_3), 23.2 (s, CH_2), 23.31 (s, CH_2), 32.4 (s, 2C, CH_2), 65.7 (s, C≡C), 77.9 (s, C≡C), 124.2, 125.1, 127.0, 127.5, 128.0, 129.8 (s, CH), 119.4, 124.8 (s, C), 134.4 (s, C=CH), 137.9 (s, Co–C), 186.0 (C–O), 217.0 (C=O) ppm. ^{31}P NMR (d_8-THF, 300 K) $\delta = 2.8$ ppm (s, PCH_3).

*2.2.2. Preparation of (1-carbonyl-2-oxo-1,2-diphenylethene-diyl)-[(Z)-1-phenylethinyl-2-phenylethenyl]-trans-bis(trimethylphosphine)cobalt(III) (**7**)*

Diphenylbutadiyne (160 mg, 0.79 mmol) was added to a stirred solution of *mer*-hydrido-(1-carbonyl-2-oxo-1,2-diphenylethene-diyl)tris(trimethylphosphine) cobalt (III) (**2**) (400 mg, 0.78 mmol) in 50 ml of pentane. The yellow solution gradually turned red brown within 20 min. The mixture was kept at room temperature for 18 h during which a brown precipitate formed. After filtering, the solid residue was extracted with 80 ml of ether and the solution was kept at 0 °C to afford red brown crystal **7**. Yield: 280 mg (57%); m.p. 133–135 °C (dec.). *Anal.* Calc. for $C_{37}H_{39}CoO_2P_2$ (536.59 g/mol): C, 69.81; H, 6.17. Found: C, 69.89; H, 5.96%. IR (Nujol): $v = 2133$ (C≡C); 1630 (C=O); 1590, 1568, 1520 (C=C) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 K): $\delta = 1.14$ (s, 18H, PCH_3), 6.92 (s, 1H, C=CH), 6.94–7.60 (m, 20H, CH) ppm. ^{13}C NMR ($CDCl_3$, 300 K): $\delta = 13.2$ (t, $|^{1}J(\mathrm{PC}) + {}^{3}J(\mathrm{PC})| = 26.8$ Hz, PCH_3), 76.7 (s, C≡C), 87.0 (s, C≡C), 124.2, 125.0, 126.6, 126.7, 127.0, 127.1, 127.2, 127.5, 127.7, 127.8, 128.1, 128.5, 129.8 (s, CH), 136.0 (s, C=CH), 140.6 (s, Co–C), 185.2 (C–O), 201.1 (C=O) ppm. ^{31}P NMR ($CDCl_3$, 300 K): $\delta =$ 10.3 ppm (s, PCH_3).

*2.2.3. Preparation of (1-carbonyl-2-oxo-5-phenyl-cyclohexene-diyl)-[(Z)-1-phenylethinyl-2-phenylethenyl]-trans-bis(trimethylphosphine)cobalt(III) (**8**)*

Diphenylbutadiyne (280 mg, 1.39 mmol) was added to a stirred solution of *mer*-hydrido-(1-carbonyl-2-oxo-5-phenyl-cyclohexene-diyl)tris(trimethylphosphine) cobalt(III) (**3**) (680 mg, 1.39 mmol) in 50 ml of pentane at room temperature. The orange-yellow solution gradually turned red brown during reaction for 15 h. Red brown precipitate crystallized from ether to afford brown needle crystal **8**. Yield: 350 mg (41%); m.p. 143–145 °C (dec.). *Anal.* Calc. for $C_{35}H_{41}CoO_2P_2$ (614.59 g/mol): C, 68.40; H, 6.72. Found: C, 68.28; H, 6.77%. IR (Nujol): $v = 2138$ (C≡C), 1664, 1623 (C=O); 1592, 1542 (C=C) cm^{-1}. ^{1}H NMR (d_8-THF, 300 K): $\delta = 1.19$ (t′, $|^{2}J(\mathrm{PH}) + {}^{4}J(\mathrm{PH})| = 7.8$ Hz, 18H, PCH_3), 1.83-2.59 (m, 6H, CH_2), 2.69 (m, 1H, CH), 6.79 (t, $^{4}J(\mathrm{PH}) = 4.2$ Hz, 1H, C=CH), 7.01–7.69 (m, 15H, CH) ppm. ^{13}C NMR (d_8-THF, 300 K): $\delta = 10.8$ (m, PCH_3), 31.2 (s, CH_2), 32.8 (s, CH_2), 32.9 (s, CH_2), 41.9 (s, CH), 78.2 (s, C≡C), 104.39 (s, C—C=O), 125.5 (s, Co–C), 125.0, 125.8, 126.0, 127.0, 127.8, 128.3, 128.4, 128.8, 130.6 (s, CH), 135.0 (s, C=CH), 120.3, 138.6, 147.0 (s, C), 186.4 (s, C–O), 217.8 (s, C=O) ppm. ^{31}P NMR (d_8-THF, 213 K): $\delta = 12.5$ (s) ppm.

*2.2.4. Preparation of (1-carbonyl-2-oxo-5-tert-butyl-cyclohexene-diyl)-[(Z)-1-phenylethinyl-2-phenylethenyl]-trans-bis(trimethylphosphine)cobalt(III) (**9**)*

Diphenylbutadiyne (300 mg, 1.49 mmol) was added to a stirred solution of *mer*-hydrido(1-carbonyl-2-oxo-5-*tert*-butyl-cyclohexene-diyl)tris(trimethylphosphine) cobalt(III) (**4**) (680 mg, 1.46 mmol) in 50 ml of pentane at room temperature. After 15 h, the solid precipitate crystallized from ether to afford brown crystal **9**. Yield: 320 mg (36%); m.p. 139–141 °C (dec.). *Anal.* Calc. for $C_{33}H_{45}CoO_2P_2$ (594.60 g/mol): C, 66.66; H, 7.63. Found: C, 66.50; H, 7.58%. IR (Nujol): $v = 2140$ (C≡C); 1660, 1627 (C=O); 1592, 1544, 1508 (C=C) cm^{-1}. ^{1}H NMR (d_8-THF, 300 K): $\delta = 1.04$ (t′, $|^{2}J(\mathrm{PH}) + {}^{4}J(\mathrm{PH})| = 7.8$ Hz, 18H, PCH_3), 0.79 (s, 9H, $C(CH_3)_3$), 1.71–2.19 (m, 6H, CH_2), 2.27 (m, 1H, CH), 6.67 (t, $^{4}J(\mathrm{PH}) = 4.2$ Hz 1H, C=CH), 6.67–7.56 (m, 10H, CH) ppm. ^{13}C NMR (d_8-THF, 300 K): $\delta = 10.7$ (m, PCH_3), 27.3 (s, C, $C(CH_3)_3$), 32.3 (s, $C(CH_3)_3$), 25.4, 33.5 (s, CH_2), 44.1 (s, CH), 77.6 (s, C≡C), 135.1 (s, C=CH), 124.9, 125.8, 127.79, 128.3, 128.7, 130.6 (s, CH) 120.0, 125.5, 138.6 (s, C) ppm. ^{31}P NMR (d_6-Aceton, 300 K): $\delta = 2.8$ ppm (m).

*2.2.5. Preparation of (3-tert-butyl-5-methyl-2-oxobenzoyl)-[(Z)-1-phenylethinyl-2-phenylethenyl]-trans-bis(trimethylphosphine)cobalt(III) (**10**)*

Diphenylbutadiyne (210 mg, 1.04 mmol) was added to a stirred solution of *mer*-hydrido(3-*tert*-butyl-5-methyl-2-oxobenzoyl)tris(trimethylphosphine)cobalt(III) (**5**) (500 mg, 1.04 mmol) in 50 ml of pentane as described above to afford red crystal **10**. Yield: 180 mg (28%); m.p. 130–132 °C (dec.). *Anal.* Calc. for $C_{34}H_{43}CoO_2P_2$ (604.59 g/mol): C, 67.55; H, 7.17. Found: C, 67.48; H, 6.90%. IR (Nujol): $v = 2163$ (C≡C), 1598, 1565, 1529 (C=C) cm^{-1}. ^1H NMR($CDCl_3$, 300 K): $\delta = 0.98$ (t′, $|^2J(PH) + {}^4J(PH)| = 7.0$ Hz, 18H, PCH_3), 1.53 (s, 9H, $C(CH_3)_3$), 2.21 (s, 3H, CH_3), 6.90 (s, 1H, C=CH), 6.90–7.90 (m, 12H, CH) ppm. ^{13}C NMR ($CDCl_3$, 300 K): $\delta = 11.1$ (t′, $|^1J(PC) + {}^3J(PC)| = 26.6$ Hz, PCH_3), 19.9 (s, CH_3), 28.9 (s, $C(CH_3)_3$), 34.2 (s, $C(CH_3)_3$), 76.7 (s, C≡C), 85.1 (s, C≡C), 137.2 (s, C=CH), 117.6, 125.0, 125.2, 127.7, 128.0, 128.1, 130.1 (s, CH), 120.1, 124.2, 130.2, 132.6, 137.2, 137.8 (s, C), 174.6 (s, C–O), 192.0 (s, C=O) ppm. ^{31}P NMR ($CDCl_3$, 300 K): $\delta = 4.4$ ppm (s).

*2.2.6. Preparation of mer-carbonyl-(1-carbonyl-2-oxo-1,2-diphenyl-diyl)-[(Z)-1-phenylethinyl-2-phenylethenyl]-trans-bis(trimethylphosphine)cobalt(III) (**11**)*

A 30 ml diethyl ether solution of sample **7** (200 mg, 0.31 mmol) was continuously stirred under 1 bar of CO at room temperature. The red solution instantly turned yellow. After keeping for 2 h, the solution was filtered and condensed to afford yellow crystal **11** at 0 °C. Yield: 78 mg (37%); m.p. 133–135 °C (dec.). IR (Nujol): $v = 2143$ (C≡C), 2023 (C≡O), 1613 (C=O), 1594, 1535 (C=C) cm^{-1}. ^1H NMR($CDCl_3$, 300 K): $\delta = 1.41$ (t′, $|^2J(PH) + {}^4J(PH)| = 8.2$ Hz, 18H, PCH_3), 7.02 (s, 1H, C=CH), 7.03–7.82 (m, 20H, CH) ppm. ^{13}C NMR ($CDCl_3$, 300 K): $\delta = 13.0$ (m PCH_3), 76.7 (s, C≡C), 124.5, 124.8, 125.3, 127.0, 127.5, 128.0, 129.9, 130.1 (s, CH),137.0 (s, C=CH) 140.6 (m, Co–C), 185.2 (s, C–O), 201.1 (s, C=O) ppm. ^{31}P NMR ($CDCl_3$, 300 K): $\delta = 9.9$ ppm (s).

2.2.7. Crystal structure analyses

Crystal data for compounds **6** and **11** are presented in Tables 1 and 2. The single crystals were mounted on a Bruker AXS P4 diffractometer. Reflections were measured using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods. Full-matrix least-squares refinement based on F^2 was used. All non-hydrogen atoms were anisotropically refined. Program such as SHELXTL was used.

Table 1
Crystal data for compound **6**

Empirical formula	$C_{29}H_{37}CoO_2P_2$
Formula mass	538.46
Crystal size (mm)	$0.49 \times 0.46 \times 0.11$
Crystal system	monoclinic
Space group	$P2(1)/c$
a (Å)	24.239(7)
b (Å)	10.161(3)
c (Å)	11.964(3)
β (°)	103.084(5)
V (Å^3)	2870.3(14)
Z	4
D_{calc} (g cm^{-3})	1.246
μ (Mo Kα) (mm^{-1})	0.732
Temperature (K)	273(2)
Data collection range (°)	$2.18 \leqslant 2\theta \leqslant 25.03$
h	$-28 \leqslant h \leqslant 25$
k	$-12 \leqslant k \leqslant 11$
l	$-14 \leqslant l \leqslant 10$
Number of reflections measured	14358
Number of unique data [R_{int}]	5055 [0.0610]
Parameters	307
Goodness-of-fit on F^2	1.021
R_1 [$I > 2\sigma(I)$]	0.0561
wR_2 (all data)	0.1692

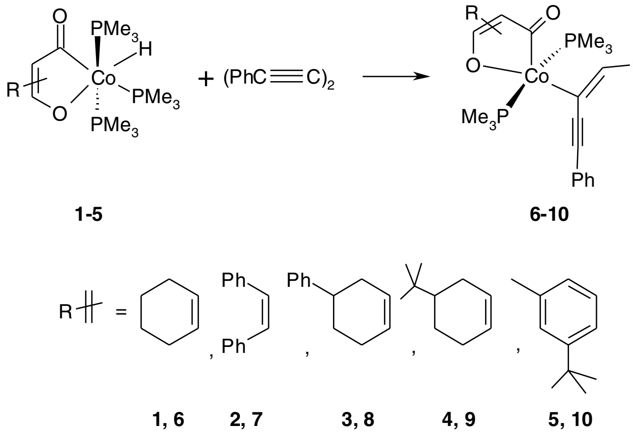
Table 2
Crystal data for compound **11**

Empirical formula	$C_{76}H_{78}Co_2O_6P_4$
Formula mass	1329.12
Crystal size (mm)	$0.89 \times 0.40 \times 0.15$
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.5755(17)
b (Å)	12.886(2)
c (Å)	30.823(6)
α (°)	80.557(2)
β (°)	89.987(3)
γ (°)	68.158(2)
V (Å^3)	3474.8(11)
Z	2
D_{calc} (g cm^{-3})	1.270
μ (Mo Kα) (mm^{-1})	0.620
Temperature (K)	293(2)
Data collection range (°)	$1.73 \leqslant 2\theta \leqslant 25.00$
h	$-8 \leqslant h \leqslant 11$
k	$-14 \leqslant k \leqslant 15$
l	$-36 \leqslant l \leqslant 33$
Number of reflections measured	17759
Number of unique data [R_{int}]	11987 [0.0331]
Parameters	806
Goodness-of-fit on F^2	1.047
R_1 [$I > 2\sigma(I)$]	0.0695
wR_2 (all data)	0.1714

3. Results and discussion

3.1. Mono-insertion reaction with diphenylbutadiyne

Reactions of 2-acyl enolato hydrido cobalt(III) complexes **1**–**4** and 2-acyl phenolato hydrido cobalt(III) complex **5** with diphenylbutadiyne form five-coordinatively unsaturated acyl vinyl cobalt(III) complexes **6**–**10** containing 1,4-diphenylbut-1-en-3-yn-2-yl ligand, η^1-C(C≡CPh)=CHPh, by mono-insertion of the diyne into the Co–H bond accompanying one trimethylphosphine ligand leaving. The reactions proceeded at room temperature in pentane extending over 15–18 h.



(1)

Crystals or powders **6–10** were obtained from diethyl ether or pentane solution. In infrared spectra, typical signals for the vibration of (Co–H) bond are absent and the valence vibration of C≡C bonds (2133–2141 cm^{-1}) are observed, indicating that mono-insertion reactions took place.

From ^{1}H NMR spectroscopy, we know that a pseudotriplet between 0.98 and 1.14 ppm with strong coupling $|^{2}J(\mathrm{PH}) + {}^{4}J(\mathrm{PH})| = 7.0$–$7.8$ Hz is recorded for two *trans*-$\mathrm{PMe_3}$ ligands. Signals of vinylic proton of the alkenyl group are found in the region of 6.67–6.79 ppm. In ^{31}P NMR spectrum, a singlet is detected indicating two trimethylphosphine ligands in the same chemistry surroundings. The magnetic properties of these compounds confirm that these complexes have a square pyramidal configuration with two *trans*-trimethylphosphine ligands in the square plane. This conjecture is verified through X-ray single crystal diffraction. By crystallization from pentane, single crystals of **6** for X-ray diffraction analysis were obtained.

The molecular structure of compound **6** is shown in Fig. 1. The structure is similar to that of (3-*tert*-butyl-5-methyl-2-oxobenzoyl)(1-ethoxocarbonyl-1-vinyl)-*trans*-bis(trimethylphosphine)cobalt(III) [8]. The cobalt atom centers in the square plane of the square pyramidal and attains a coordination with two equatorial phosphor atoms of *trans*-trimethylphosphine ligands and a carbon atom of vinyl group and an oxygen atom of phenoxy group. The carbon atom of acyl group is situated at the apex point of the square pyramidal geometry.

Angular distortion of C1–Co–C8 = 105.2° may result from the bulky σ-phenylvinyl ligand. The chelating acylphenolato ligand with a chelate-bite angle C1–Co1–O1 = 86.2° spans apical and basal positions in the square pyramid. The phenyl ring (C10–C15) in phenyl vinyl group is rotated out of the square plane (P1C8P2O1) with a dihedral angle of 116.3° and the phenyl group (C18–C23) in phenyl alkynyl moiety is rotated out of the square plane (P1C8P2O1) with a dihedral angle of 93.3°. A folding angle of 98.1° is observed between these two phenyl rings. C1–O2 bond length (1.219(6) Å) is slightly shorter than previously reported acyl cobalt complexes. Co–C8 bond length (1.917(5) Å) falls in the typical range for σ-vinyl complexes. Co–C1 with 1.909 Å is shorter than that of the six-coordinate hydrido acyl phenolato cobalt(III) complexes with Co–C1 from 1.925 to 1.952 Å [9]. Displacement of the Co atom is toward the acyl group. These effects can be explained by a stronger Co–C bonding interaction without the sixth ligand in the *trans*-position of acyl group, which would normally compete with alkyl for the metal d_{z^2} orbital. The metallation steers at position 2 of the

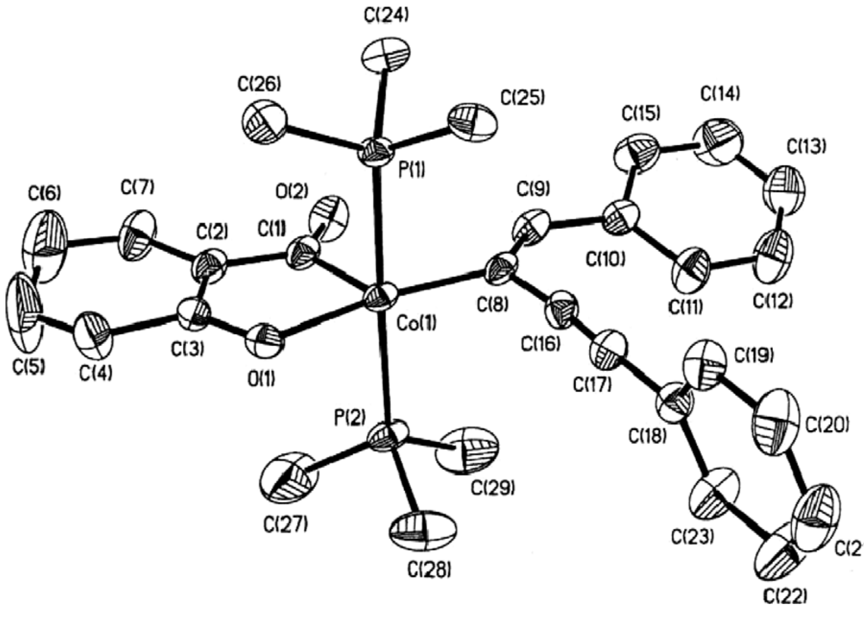


Fig. 1. Molecular structure of **6**: selected bond distances (Å) and bond angles (°): Co1–C1 1.909(6), Co1–C8 1.917(5), Co1–O1 1.953(4), Co1–P1 2.220(1), Co1–P2 2.231(2), C1–O2 1.219(6), C8–C9 1.350(7), C16–C17 1.206(7); C1–Co–O1 86.2(2), C1–Co1–P1 89.6(2), C1–Co1–P2 92.5(2), C1– Co1–C8 105.2(2), P1–Co1–P2 177.93(6), O1–Co1–C8 168.5(2), C8–C16–C17 174.1(6), C16–C17–C18 174.1(5).

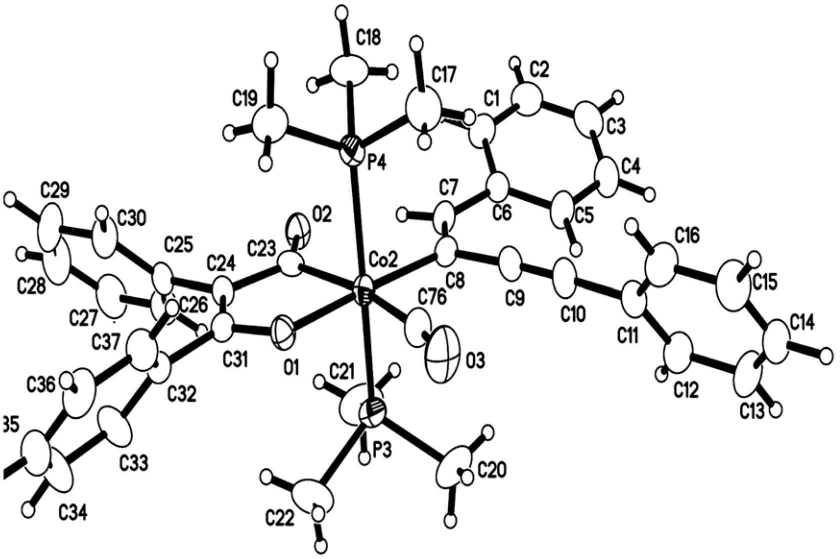
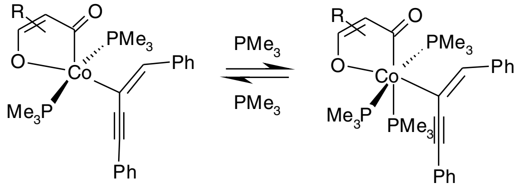


Fig. 2. Molecular structure of **11**: selected bond distances (Å) and bond angles (°): Co2–C76 1.886(5), Co2–C8 2.008(4), Co2–C23 1.974(4), Co2–O1 1.967(3), Co2–P3 2.222(1), Co2–P4 2.213(1), C1–O2 1.219(6), C6–C7 1.477(6), C7–C8 1.352(6), C8–C9 1.415(6), C9–C10 1.207(6), C10–C11 1.427(6), C23–Co2–C76 165.1(2), C8–Co2–O1 176.0(2), P4–Co2–P3 167.50(6), C76–Co2–O1 81.60(2), C76–Co2–C8 94.4(2), Co2–C76–O3 170.1(5), C8–Co2–C23 100.5(2), C23–Co2–O1 83.6(2) C8–C9–C10 175.4(5), C9–C10–C11 173.1(5).

C-chain of the butadiyne. It is supposed that the regioselectivity of the insertion reaction with diphenylbutadiyne is similar to that with bis(trimethylsilyl)butadiyne in view of steric factor.

It is interesting to note that a reversible 16–18 electron interconversion is present as shown in Eq. (2). Treatment of **6**–**10** with an excess of PMe_3 at room temperature proceeded smoothly monitored by the change in the red color of the solution to yellow. But at room temperature only the five coordinated acyl vinyl cobalt(III) complexes were isolated. In the case of insertion reaction with bis(trimethylsilyl)butadiyne [7], the reversible 16–18 electron interconversion is also present at lower temperature, and hexa-coordinated acyl vinyl cobalt(III) complexes were successfully isolated at room temperature.

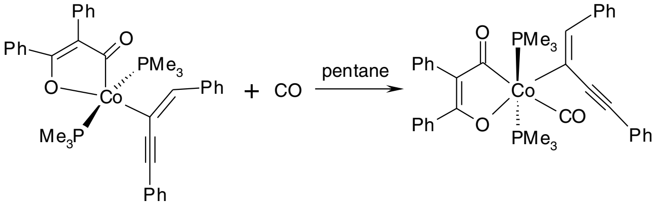


6 - 10

(2)

3.2. Reaction with carbon monoxide

Complexes **1**–**5** are formal 16-electron species. They are stable in solid state. But in solution they are highly reactive toward CO. Carbon monoxide easily coordinates to 16-electron acyl cobalt(III) complexes, leading to the formation of coordinatively saturated configurations. The reaction of acyl cobalt(III) complex **7** with carbon monoxide proceeds smoothly in diethyl ether solution under 1 bar of CO at room temperature. The reaction takes place instantly accompanying obvious change of the color of the solution from red-brown to yellow.



7 **11**

(3)

A strong infrared absorption 2023 cm^{-1} shows the existence of a terminal carbonyl ligand. ^1H NMR spectroscopy indicates a pseudo-triplet by 1.41 ppm with strong coupling $|^2J(PH) + ^4J(PH)| = 8.2$ Hz, which is recorded for the two *trans*-PMe_3 ligands.

By re-crystallization from pentane at 4 °C, single crystals of **11** as yellow plate for an X-ray diffraction analysis were obtained. A view of the molecular geometry is shown in Fig. 2 with selected bond distances and bond angles. The molecular structure of **11** (Fig. 2) shows an expected octahedral configuration of monocarbonyl acyl cobalt(III) complex with the CO group in a position opposite to the acyl function and two *trans* trimethylphosphine ligands in axial position. This structure is related to that of *mer*-carbonyl-(1-carbonyl-2-oxo-cyclohexen-diyl)-[(*Z*)-1-trimethylsilylethinyl-2-trimethylsilylethenyl]-*trans*-bis(trimethylphosphine) cobalt(III) [7]. As a result of *trans*-influence of acyl unit, distance Co2–C76 with 1.886(5) Å in *trans*-position to acyl group is considerably longer than the corresponding bond (1.782(9) Å) in cobalt(III) complex, $[CpCo(dppe)\text{-}CO](PF_6)_2 \cdot (CH_3)_2CO$ [11]. Under the experimental conditions, insertion of CO into the Co–C bond was not observed.

4. Conclusion

We have reported the formation of five new five-coordinate acyl vinyl cobalt(III) complexes $Co\{\eta^1\text{-}C(C\equiv CPh)=CHPh\}[C(O)-C=C-O\ ]L_2$ ($L = PMe_3$) (**6**–**10**) through the formal insertion of diphenylbutadiyne into Co–H function of *mer*-octahedral hydrido acyl(phenolato)-cobalt(III) complexes. These complexes are characterized with NMR and IR spectroscopy. The complexes are diamagnetic. One square pyramidal structure of complex **6** was confirmed by X-ray crystallography. The complexes are stable in solid state. In solution, hexa-coordinate acyl vinyl carbonyl cobalt(III) complex **11** was approved through the reaction of complex **7** with CO and the structure of complex **11** was determined by X-ray method.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure described in this publication have been deposited as supplementary material with the Cambridge Crystallographic Data Centre. Deposition number is CCDC-273386 for **6** and CCDC-273395 for **11**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.03.029.

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