Inorganica Chimica Acta, 218 (1994) 143–149

Preparation and crystal structure of *anti*-(η^3:η^5-azulene)pentakis-(trimethylphosphine)dicobalt. Reactions with carbon monoxide and solution dynamics

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(Received October 26, 1993; revised December 13, 1993)

Abstract

Azulene dicobalt complexes $[anti\text{-}1,2,3,9,10\text{-}\eta^5\text{:}4,5,6\text{-}\eta^3\text{-}C_{10}H_8]Co_2(CO)_n(PMe_3)_{5-n}$ ($n=0$ (**1**); 1 (**2**); 3 (**3**)) have been synthesized by reaction of olefintris(trimethylphosphine)cobalt(0) with azulene under ambient conditions followed by treatment with stoichiometric amounts or excess of carbon monoxide, respectively. X-ray structural data for **1** show a cyclopentadienyl-type η^5-coordination of a $Co(PMe_3)_2$ group and an η^3-allyl coordination of a $Co(PMe_3)_3$ group to the five- and seven-membered rings of azulene, respectively, while a vinylic C=C bond remains uncoordinated. Temperature dependent proton resonances of the azulene ligand in **1**–**3** are explained by Co(ligand)$_3$ groups fluctuating between two equivalent sites above the seven-membered ring.

Key words: Crystal structures; Cobalt complexes; Azulene complexes; Phosphine complexes; Carbonyl complexes; Dinuclear complexes

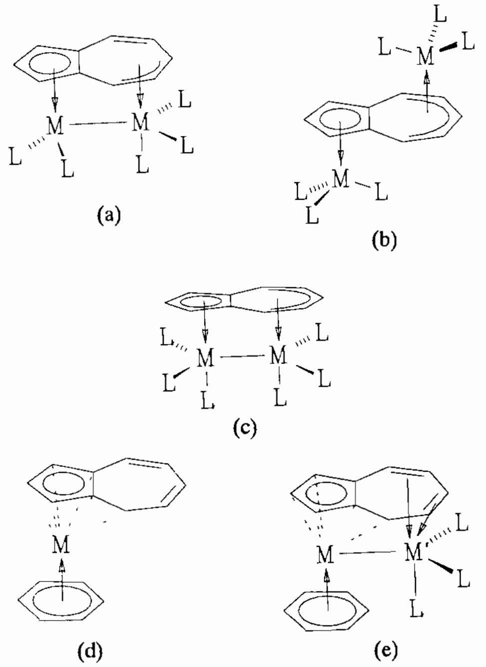
Introduction

π-Coordinated ligands attached to $Co(PMe_3)_3$ fragments are known to stabilize the paramagnetic valence state of cobalt(0). Examples with olefins [1, 2] or olefin-type anthracene ligands [3] can be regarded as stable organometallic radicals with the unpaired electron in a 2b molecular orbital of purely metal character as shown for the C_{3v} model $Co(C_2H_4)(PH_3)_3$ [4].

Diolefins when coordinated to $Co(PMe_3)_2$ fragments [5] give rise to distorted ground state structures of complexes [6], but although spin-pairing is easily achieved by reaction with CO or NO, radical chain reactions (with ethene or styrene) are not initiated.

Antiferromagnetic coupling of two cobalt (d^9) centres is mediated through the norbornadiene π-system [7] while butadiene effects oxidative coupling to give a bis(π-allyl)dicobalt(I) complex [5]. This C,C coupling reaction is likely to proceed by single-electron transfer followed by C-radical dimerization.

A similar reaction sequence can be envisaged for the azulene ligand. Its blue colour is due to a low-



Scheme 1. Known types of π-azulene transition-metal complexes. (a) M=Fe, Ru [10]; (b) M=Mn [11]; (c) M=Cr, Mo [12]; (d) M=Mo [13]; (e) M=Mo, M'=Cr, Mo, W [14]; L=CO.

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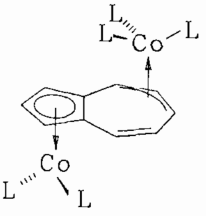
SSDI 0020-1693(94)03803-V

lying singlet state [8]. Indeed, C,C coupling reactions of azulene have been induced by metal coordination in some cases [9], but more frequently metal to metal bonds are formed instead, to give *syn-facial* complexes (Scheme 1) [10–14]. All known types of azulene complexes are stabilized by carbon monoxide or π-coordinated aromatic ligands with an occasional phosphine among them as in Mo_2(7-isopropyl-1,4-dimethyl-azulene)$(CO)_5(PEt_3)$ [15]. No azulene complex of cobalt could be obtained from $Co_2(CO)_8$ [16]. We found that azulene coordination to trimethylphosphinecobalt(0) fragments causes complete spin-pairing of two metal (d^9) centres to give diamagnetic dicobalt complexes of azulene containing phosphine or phosphine and carbonyl ligands. Dynamic ^1H NMR spectra revealed fluxional behaviour of the CoL_3 moiety attached to the seven-membered ring in an *anti-facial* position with respect to the cyclopentadienyl-type coordinated CoL_2 group.



Experimental

General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Microanalyses were carried out by Dornis & Kolbe, microanalytical laboratory, Mülheim (Germany). Trimethylphosphine was prepared from triphenylphosphite and methylmagnesium chloride [17]. Azulene (Aldrich) was freshly sublimed *in vacuo* prior to syntheses. IR spectra (4000–400 cm^{-1}) as obtained from nujol mulls between KBr windows were recorded on a Perkin-Elmer type 397 spectrophotometer. ^1H NMR spectra were obtained from a Bruker WM 300 (300 MHz) spectrometer equipped with a low-temperature unit that was calibrated with a standard methanol sample. Calculation of dynamic NMR spectra [18] remained incomplete either because of low resolution of lines (**1**) or because of too small a range of temperature (**2** and **3**). Melting points as determined in capillaries sealed under argon are uncorrected.

Procedures

Synthesis of [anti-1,2,3,9,10-η^5:4,5,6-η^3-azulene]$Co_2(PMe_3)_5$ (1)

(a) To 0.38 g (1.2 mmol) $Co(COD)(PMe_3)_2$ [6] in 50 ml of pentane at −70 °C under argon was added 0.07 g (0.55 mmol) azulene. Upon warming the green mixture to 20 °C a violet solution was obtained within 40 min. After 16 h this was filtered and kept at 0 °C to give 0.26 g of violet sticklets (76%).

(b) To 0.5 g (1.4 mmol) Co(*cyclo*-C_5H_8)$(PMe_3)_3$ [1] in 70 ml of ether at −50 °C was added 0.09 g (0.7 mmol) azulene. The violet solution was kept stirring at 20 °C for 5 h. The volatiles were evaporated and the residue was extracted with 50 ml pentane over a glass-sinter disc (G 3). Crystallization at −30 °C afforded 0.39 g of dark violet sticklets (89%), decomp. > 80 °C.

Anal. Calc. for $C_{25}H_{53}Co_2P_5$ (626.4): C, 47.93; H, 8.53; P, 24.72. Found: C, 47.83; H, 8.08; P, 24.12%.

^1H NMR (300 MHz, toluene-d_8, Me_4Si external reference, δ 0) 373 K: $\delta(CH)$ 5.27 (t, $^3J(HH) = 2.5$ Hz, 1H), 4.62 (broad signal, 2H), 4.44 (broad signal, 2H), 3.91 (broad signal, 2H), 2.97 (broad signal, 1H), $\delta(PCH_3)$ 1.25 (s, 18H), 1.07 (s, 27H). 343 K: $\delta(CH)$ 5.31 (t, $^3J(HH) = 2.4$ Hz, 1H), 4.60 (broad signal), 4.45 (broad signal), 3.91 (broad multiplet), 2.97 (broad signal), $\delta(CH_3)$ 1.76 (t, $^2J(PH) = 3.7$ Hz, 18H), 1.06 (s, 27H). 295 K: $\delta(CH)$ 5.42 (broad signal), 3.93 (broad signal), 2.96 (broad signal), 1.26 (broad signal, 18H), 1.05 (broad signal, 27H). 243 K: $\delta(CH)$ 6.38 (broad signal, 1H), 5.87 (broad signal, 1H), 5.56 (broad signal, 1H), 4.16 (broad signal), 3.74 (broad signal, 1H), 3.13 (broad signal, 1H), 3.00 (broad signal, 2H), $\delta(PCH_3)$ 1.26 (broad signal, 18H), 1.04 (broad signal, 27H).

Synthesis of [anti-1,2,3,9,10-η^5:4,5,6-η^3-azulene]$Co_2(CO)(PMe_3)_4$ (2)

To 0.39 g (0.6 mmol) **1** in 50 ml of ether at −70 °C under vacuum were added 15 ml of carbon monoxide (0.6 mmol) from a gas buret. After stirring the mixture in the closed system for 16 h at 20 °C the volatiles were evaporated and the dark brown residue was dried *in vacuo* for 30 min at 20 °C. Extraction with 50 ml of pentane followed by filtration and cooling to −18 °C afforded 0.26 g of dark brown crystals (73%), m.p. 91–92 °C.

Anal. Calc. for $C_{23}H_{44}Co_2OP_4$ (578.4): C, 47.76; H, 7.67; P, 21.42. Found: C, 47.87; H, 7.81; P, 21.65%.

IR (THF solution, 2100–1500 cm^{-1}): 1898vs, $\nu(CO)$. Mass spectrum (EI, 70 °C): $m/e = 426$ ($M^+ - 2PMe_3$), 398 ($M^+ - 2PMe_3 - CO$). ^1H NMR (300 MHz, toluene-d_8, Me_4Si external reference, δ 0) 297 K: $\delta(CH)$ 6.22 (broad signal), 5.58 (broad signal), 4.94 (broad signal), 4.87 (t, $^3J(HH) = 2.4$ Hz, 1H), 4.12 (broad signal), 3.13 (s, 2H), 2.74 (multiplet, 1H) $\delta(PCH_3)$ 1.21 (d, $^2J(PH) = 8.9$ Hz, 9H), 0.94 (s, 27H). 273 K: $\delta(CH)$ 6.39 (multiplet, 1H), 5.67 (multiplet, 1H), 5.06 (s, 1H), 4.92 (s, 1H), 4.15 (s, 1H), 3.10 (s, 2H), 2.74 (s, 1H), $\delta(PCH_3)$ 1.19 (d, $^2J(PH) = 8.7$ Hz, 9H), 0.92 (s, 27H). 253 K: $\delta(CH)$ 6.43 (t, $^3J(HH) = 9.0$ Hz, 1H), 5.67 (d, $^3J(HH) = 9.5$ Hz, 1H), 5.10 (s, 1H), 4.96 (s, 1H), 4.13

(s, 1H), 3.09 (s, 2H), 2.73 (s, 1H), $\delta(PCH_3)$ 1.18 (d, $^2J(PH) = 8.6$ Hz, 9H), 0.90 (s, 27H). 223 K: 6.52 (s, 1H), 5.73 (s, 1H), 5.19 (s, 1H), 5.04 (s, 1H), 4.06 (s, 1H), 3.09 (s, 2H), 2.76 (s, 1H), $\delta(PCH_3)$ 1.14 (s, 9H), 0.88 (s, 27H). $^{31}P\{^1H\}$ NMR (121.5 MHz, toluene-d_8, H_3PO_4 external reference, δ 0) 297 K: $\delta(P)$ 15.15 (s, 1P), 6.17 (s, 3P). 233 K: 16.03 (s, 1P), 7.55 (s, 3P).

Synthesis of [anti-1,2,3,9,10-η^5:4,5,6-η^3-azulene]$Co_2(CO)_3(PMe_3)_2$ (3)

A sample of 0.32 g (0.5 mmol) of **1** in 60 ml of ether under 1 bar CO was kept stirring for 15 h at 20 °C. The brown yellow solution was evaporated to give a brown oily residue. This was dissolved in 50 ml pentane and after filtration crystallized at 0 °C to give 0.19 g of dark brown crystals (77%), m.p. 99–100 °C.

Anal. Calc. for $C_{19}H_{26}Co_2O_3P_2$ (482.2): C, 47.32; H, 5.43. Found: C, 47.75; H, 5.76%.

IR (THF solution, 2100–1500 cm^{-1}): 1980vs, 1950sh, 1925vs, 1905vs, ν(CO). Mass spectrum (FI, 70 °C): $m/e = 482$ (M^+), 454 ($M^+ - CO$), 426 ($M^+ - 2CO$), 406 ($M^+ - PMe_3$). ^1H NMR (300 MHz, toluene-d_8, Me_4Si external reference, δ 0) 297 K: $\delta(CH)$ 6.09 (broad signal, 1H), 5.70 (broad signal, 1H), 4.90 (broad signal, 1H), 4.70 (s, 1H), 4.58 (broad signal, 1H), 4.15 (broad signal, 1H9), 3.95 (broad signal, 1H), 3.74 (broad signal, 1H9), $\delta(PCH_3)$ 1.01 (d, $^2J(PH) = 9.1$ Hz, 9H), 0.93 (d, $^2J(PH) = 8.3$ Hz, 9H). 273 K: $\delta(CH)$ 6.11 (broad signal, 1H), 5.73 (d, $^3J(HH) = 105$ Hz, 1H), 4.93 (s, 1H), 4.72 (s, 1H), 4.57 (t, $^3J(HH) = 9.0$ Hz, 1H), 4.16 (s, 1H), 3.89 (s, 1H), 3.71 (s, 1H), $\delta(PCH_3)$ 0.97 (d, $^2J(PH) = 9.2$ Hz, 9H), 0.89 (d, $^2J(PH) = 8.3$ Hz, 9H). 253 K: $\delta(CH)$ 6.13 (t, $^2J(HH) = 9.4$ Hz, 1H), 5.74 (d, $^2J(HH) = 10.8$ Hz, 1H), 4.95 (s, 1H), 4.75 (s, 1H), 4.57 (t, $^3J(HH) = 5.5$ Hz, 1H), 4.18 (s, 1H), 3.84 (s, 1H), 3.70 (t, $^3J(HH) = 6.0$ Hz, 1H) $\delta(PCH_3)$ 0.95 (d, $^2J(PH) = 9.2$ Hz, 9H), 0.86 (d, $^2J(PH) = 8.4$ Hz, 9H). 223 K: $\delta(CH)$ 6.20 (t, $^2J(HH) = 8.8$ Hz, 1H), 5.78 (d, $^3J(HH) = 10.8$ Hz, 1H), 3.74 (s, 1H), 3.67 (s, 1H), $\delta(PCH_3)$ 0.90 (d, $^2J(PH) = 9.0$ Hz, 9H), 0.80 (d, $^2J(PH) = 8.2$ Hz, 9H).

X-ray crystal measurements

Single crystals of **1** were sealed in glass capillaries under argon. Cell dimensions were obtained from a specimen (0.20×0.33×0.45 mm) on a Nicolet R 3m/V four-circle diffractometer (Mo Kα radiation, graphite monochromator) and refined using 25 reflections with $6 \leq 2\theta \leq 26°$: $C_{25}H_{53}Co_2P_5$, $M_r = 626.4$, monoclinic, $P2_1/n$, $Z = 4$, $a = 15.379(3)$, $b = 13.838(4)$, $c = 16.629(3)$ Å, $\beta = 111.16(1)°$, $V = 3300$ Å^3, $D_{calc} = 1.261$ g cm^{-3}, $T = 296(1)$ K. A total of 6313 reflections ($3 \leq 2\theta \leq 50°$) was measured ($-18 \leq h \leq 18$, $0 \leq k \leq 16$, $0 \leq l \leq 19$). Three standard reflections were measured after every 400 reflections showing no systematic changes. After averaging of symmetry equivalent reflections ($R_{int} = 0.0318$) 5821 independent reflections remained to give 3629 with $I > 2.5\sigma(I)$. Lorentz and polarization corrections but no absorption corrections ($\mu^* t < 0.4$) were applied.

Solution and refinement of structure

The structure was solved by using direct methods (SHELXTL-PLUS); full-matrix refinement was based on F and 289 parameters. All non-hydrogen atoms were refined anisotropically. The azulene hydrogen positions were obtained from a difference Fourier synthesis, while positions of methyl-H atoms were calculated (riding model). Refinement converged to $R = R_w = 0.0489$. A final difference map exhibited maximum residuals of 0.55 e Å^{-3} (Δ/σ) < 0.001. Scattering factors and values for f' and f'' were taken from the SHELXTL-PLUS program (Nicolet 1987).

Results and discussion

Molecular compounds of zerovalent cobalt CoL_3L' ($L = PMe_3$, $L' =$ olefin, PMe_3) are slowly decomposed *in vacuo* by dissociation and removal of ligands, that cannot stabilize a 15 electron species at 20 °C. In these equilibria azulene selectively displaces olefins.

$$2Co(C{=}C)(PMe_3)_3 + C_{10}H_8 \longrightarrow \underset{\mathbf{1}}{(C_{10}H_8)Co_2(PMe_3)_5} + PMe_3 + C{=}C \quad (1)$$

$C{=}C = C_2H_4$, C_3H_6, *cyclo*-C_5H_8

The stoichiometry of eqn. (1) is strictly followed and in particular **1** is inert towards excess olefincobalt(0) complex. *In vacuo* **1** does not release phosphine prior to thermal decomposition above 78 °C. When η^5-coordination of both azulene rings is attempted in a synthesis according to eqn. (2) elemental cobalt is deposited in order to provide the fifth phosphine ligand for **1**.

$$5Co(COD)(PMe_3)_2 + 2C_{10}H_8 \longrightarrow 2\mathbf{1} + 5COD + Co \quad (2)$$

COD = 1,5-cyclooctadiene

1 is freely soluble in ether and hydrocarbon solvents. From pentane violet–red sticklets are crystallized that are sensitive to oxygen and moisture. Under argon at 80 °C decomposition is recognized from the blue colour of free azulene.

In the mass spectrometer (EI, 75 °C) several side reactions proceed. Fragments at $m/e = 520$ ($Co_2(C_{10}H_8)(PMe_2)_2(PMe_3)_2^+$) and 444 ($Co_2(C_{10}H_8)(PMe_2)_2(PMe_3)^+$) could originate from a μ-phosphido species with a *syn-facial* coordination mode.

All fragments of $Co_2(\mu\text{-}PMe_2)_2(PMe_3)_4$ [19] ($m/e=544$, 468...) are also present while only $m/e=474$ $[Co_2(C_{10}H_8)(PMe_3{}^+)]$ can be directly correlated with the parent molecule **1**. $m/e=374$ $[Co_2(C_{10}H_8)_2{}^+]$ and 315 $[Co(C_{10}H_8)_2{}^+]$ could indicate a pathway for azulene dimerization. In the IR spectrum (nujol solution) an asymmetric stretching mode of $(sp^2)CH$ absorbs at 3090 cm^{-1} while a medium intensity band at 1575 cm^{-1} can be assigned to $\nu(C{=}C)$ of an uncoordinated olefin function. An *anti*-η^5,η^3 coordination mode was assessed by X-ray crystal structure determination.

Molecular structure of $(C_{10}H_8)Co_2(PMe_3)_5$ *(1)*

Figure 1 gives a perspective view of the molecule **1**. Two *anti-facial* trimethylphosphinecobalt groups are coordinated to an azulene ligand. Above the centre of the C_5 sector of the aromatic system acting as a cyclopentadienyl-type 6-electron donor, is attached a $Co(PMe_3)_2$ group that attains 18 electrons for the metal (d^8) valence shell. In the C_7 sector a vinylic C=C bond (C4–C5 = 1.369(14) Å) is not coordinated to the metal while the atoms C1, C2 and C3 form a π-allyl system that accommodates a $Co(PMe_3)_3$ group, again with an 18-electron count for cobalt (d^8). Only C2 is slightly bent out of the azulene plane and away from Co1. CoP distances at Co1 are of the expected order (2.18–2.20 Å) while those at Co2 are distinctly shorter. The structural cone angle of trimethylphosphine comes out at 97–100° as in the structure of $Co(C_6H_3)(C_2H_4)(PMe_3)_3$ [20] with the narrowest angle P4Co2P5 = 97.2(1)°.

The bonding situation closely resembles other η^5-cyclopentadienyl and η^3-allyl metal complexes and is best described by an azulene dianion coordinated to two trimethylphosphinecobalt(I) fragments.

Fractional atomic coordinates for the non-hydrogen atoms are given in Table 1; bond distances and angles are given in Table 2.

Reactions with carbon monoxide

Generally complexes of low-valent cobalt containing both phosphine and carbonyl ligands are spontaneously formed by substitution of pure carbonyl or phosphine complexes [3, 21]. We have therefore tested substitution of phosphine ligands in **1** by carbon monoxide in order to learn how far towards the inaccessible (azulene)-$Co_2(CO)_5$ we can advance.

Stoichiometric control is necessary in order to obtain a monocarbonyl derivative **2** according to eqn. (3) as one of two possible isomers.

$$\mathbf{1} + CO \longrightarrow \underset{\mathbf{2}}{(C_{10}H_8)Co_2(CO)(PMe_3)_4} + PMe_3 \qquad (3)$$

$$\mathbf{1} + CO(\text{excess}) \longrightarrow \underset{\mathbf{3}}{(C_{10}H_8)Co_2(CO)_3(PMe_3)_2} + 3PMe_3 \qquad (4)$$

Excess carbon monoxide according to eqn. (4) selectively gives **3** as one of three possible isomers. No further substitution of phosphine ligands could be thermally achieved under 1 bar CO. Crystals of **2** and **3**

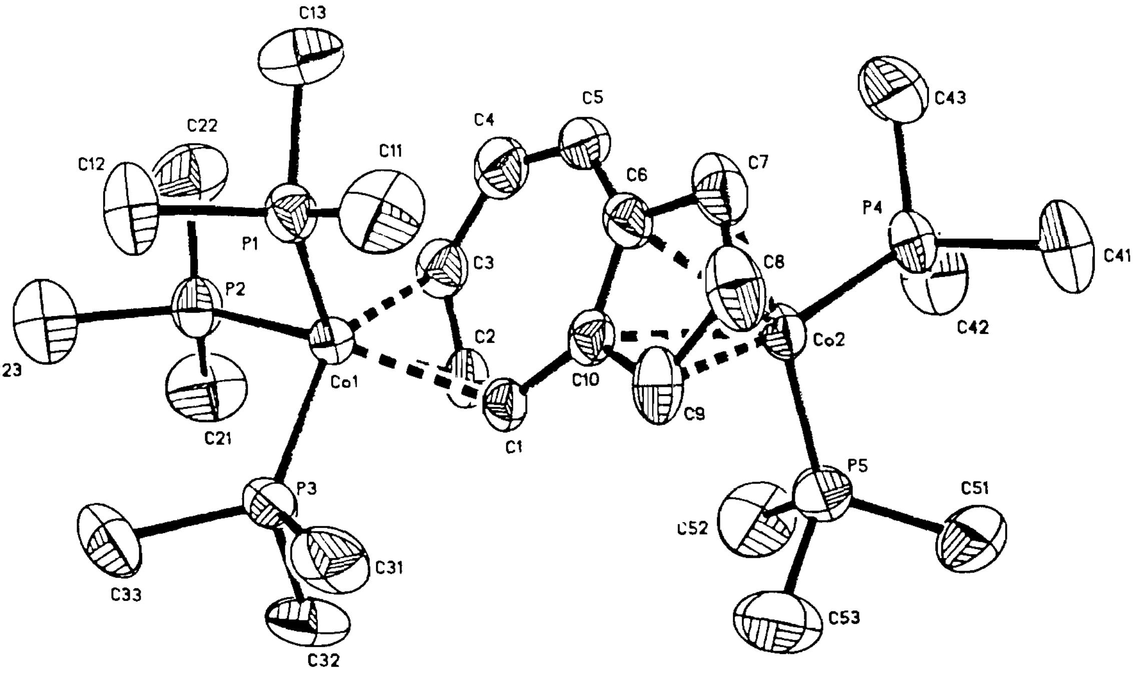


Fig. 1. Molecular structure of **1** (ORTEP plot) and atom numbering.

TABLE 1. Fractional atomic coordinates for non-hydrogen atoms with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Co1	0.4648(1)	0.7864(1)	0.2777(1)	0.031(1)
Co2	0.5962(1)	0.4490(1)	0.2534(1)	0 039(1)
P1	0.4962(2)	0.8392(2)	0.1659(2)	0.043(1)
P2	0.3459(2)	0.8763(2)	0.2727(2)	0 048(1)
P3	0.5738(2)	0.8538(2)	0.3861(2)	0.045(1)
P4	0.5352(2)	0.3167(2)	0.1955(2)	0.047(1)
P5	0.6386(2)	0 4029(2)	0.3833(2)	0.053(1)
C1	0.5383(6)	0.6546(6)	0.3197(5)	0.038(3)
C2	0.4450(6)	0.6584(6)	0.3204(6)	0.043(4)
C3	0.3681(7)	0.6677(6)	0.2404(6)	0.049(4)
C4	0.3545(7)	0.6215(7)	0.1570(7)	0.058(4)
C5	0.4152(8)	0.5727(7)	0.1283(6)	0.054(4)
C6	0.5147(7)	0.5640(6)	0.1749(6)	0.045(4)
C7	0.5808(9)	0.5198(7)	0 1406(7)	0.058(5)
C8	0.6734(8)	0.5349(7)	0.1990(7)	0.059(5)
C9	0.6668(7)	0.5799(6)	0.2742(7)	0 049(4)
C10	0.5689(6)	0.6012(6)	0.2581(5)	0.038(3)
C11	0 6020(8)	0.7976(9)	0.1475(7)	0.072(5)
C12	0.5131(11)	0.9703(7)	0.1570(8)	0.055(8)
C13	0.4112(8)	0.8203(9)	0.0571(6)	0.076(5)
C21	0.2984(8)	0.8517(10)	0.3576(8)	0.086(6)
C22	0.2382(7)	0.8689(10)	0.1788(7)	0.084(6)
C23	0.3511(9)	1.0090(9)	0.2800(12)	0.063(9)
C31	0.6953(7)	0.8342(8)	0.3962(7)	0.064(4)
C32	0.5770(8)	0.8126(9)	0.4936(6)	0.072(5)
C33	0.5829(9)	0.9855(8)	0.4083(8)	0.094(6)
C41	0.6134(8)	0.2216(7)	0.1867(8)	0.075(6)
C42	0.4619(8)	0.2461(8)	0.2393(9)	0 080(6)
C43	0.4526(9)	0.3203(8)	0.0843(7)	0 088(6)
C51	0.6827(8)	0.2804(8)	0.4175(7)	0.073(5)
C52	0.5519(10)	0.4113(11)	0.4334(8)	0.091(7)
C53	0.7342(10)	0 4683(10)	0.4616(8)	0 096(7)

[a]Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Important distances (Å) and angles (°) of **1**

Bond distances			
Co1–C2	1.974(8)	Co2–P5	2.117(3)
Co1–C1	2.128(8)	C1–C2	1.441(12)
Co1–C3	2.153(9)	C2–C3	1.431(13)
Co1–P1	2.206(3)	C3–C4	1.472(14)
Co1–P2	2.190(3)	C4–C5	1.369(14)
Co1–P3	2.178(3)	C5–C6	1.450(14)
Co2–C8	2.102(9)	C6–C7	1.468(13)
Co2–C7	2.053(10)	C7–C8	1.420(15)
Co2–C9	2.076(9)	C8–C9	1.433(13)
Co2–C6	2.151(9)	C9–C10	1.461(12)
Co2–C10	2.155(8)	C10–C1	1.471(11)
Co2–P4	2.123(3)	C10–C6	1.428(12)
Bond angles			
C3–Co1–C1	70.7(3)	C6–Co2–P5	137.7(3)
C2–Co1–C1	40.9(3)	C7–Co2–P5	165.4(3)
C3–Co1–C2	40.3(3)	C8–Co2–P5	126 6(3)
P2–Co1–P1	102.4(1)	C9–Co2–P5	98.3(3)
P3–Co1–P1	102.6(1)	C10–Co2–P5	104.5(2)
P3–Co1–P2	99.8(1)	C3–C2–C1	119.2(8)
C1–Co1–P1	135 2(3)	C4–C3–C2	128.7(9)
C2–Co1–P1	108.0(2)	C10–C1–C2	126.4(8)
C3–Co1–P1	110.4(3)	C5–C4–C3	131.3(9)
C1–Co1–P2	146.9(2)	C6–C5–C4	125.1(9)
C2–Co1–P2	106.7(3)	C10–C6–C5	128.5(9)
C3–Co1–P2	86.6(3)	C6–C10–C1	129.4(8)
C1–Co1–P3	86.4(2)	C9–C8–C7	106.9(9)
C2–Co1–P3	105.0(3)	C8–C7–C6	109.7(9)
C3–Co1–P3	144.1(3)	C10–C9–C8	108.7(9)
C6–Co2–P4	107.3(3)	C9–C10–C6	107.9(8)
C7–Co2–P4	96.3(3)	C10–C6–C7	106.4(9)
C8–Co2–P4	121.2(3)	C7–C8–C5	125.0(9)
C9–Co2–P4	161.3(3)	C9–C10–C1	122.7(8)
C10–Co2–P4	143.0(2)		

display a dark brown colour and are less air-sensitive than **1**. In solution stability against oxygen increases with the number of carbonyl groups in the molecule while solubility in hydrocarbon or ether solvents decreases in that order.

Our attempts to synthesize a dicarbonylcobalt intermediate either by reacting **1** with two equivalents of carbon monoxide or by combining **2** and **3** have met with failure. From IR and ^{1}H NMR spectra of the red oils obtained in both experiments the presence of **2** and **3** among unknown species was recognized but no separation could be achieved.

Carbon monoxide in only one position of **2** is indicated by a strong IR absorption at 1898 cm^{-1} (νCO) and by a medium intensity band at 562 cm^{-1} (δCoCO). In the ^{1}H NMR spectrum a doublet and a slightly broadened singlet in a 1:3 intensity ratio as expected for a single phosphine and for a C_{3v} $(PH_9)_3$ spin system, respectively, are consistent only with monosubstitution at Co2 (Fig. 1), as are the two singlets at 16.03 ppm (1P) and 7.55 ppm (3P) in the ^{31}P NMR spectrum at 233 K.

The carbonyl ligands of **3** in THF solution display their stretching modes with strong bands at 1980, 1925 and 1915 cm^{-1} that correspond with CoCO deformation modes absorbing at 560, 530 and 492 cm^{-1}. In the ^{1}H NMR spectrum (see Fig. 3) two PCH_3 doublets (1:1) arise from two single phosphine ligands remaining at Co1 and Co2.

At 297 K eight broad resonances of eight azulene protons of **3** are to be assigned to the anisochronic ^{1}H nuclei at C1–C5 and C7–C9 (Fig. 1). In the same region **1** displays one sharp and two broad singlets with 1:2:1 intensities corresponding to four protons. The other four azulene protons gave extremely broad signals, while **2** exhibits seven signals (with 1:1:1:1:1:2:1 intensities) showing some fine structure (see Fig. 2). The different spectra were attributed to dynamic processes in azulene coordination.

In spite of considerable problems with large temperature gradients of solubilities the ^{1}H NMR spectra of **1**–**3** were run at variable temperature.

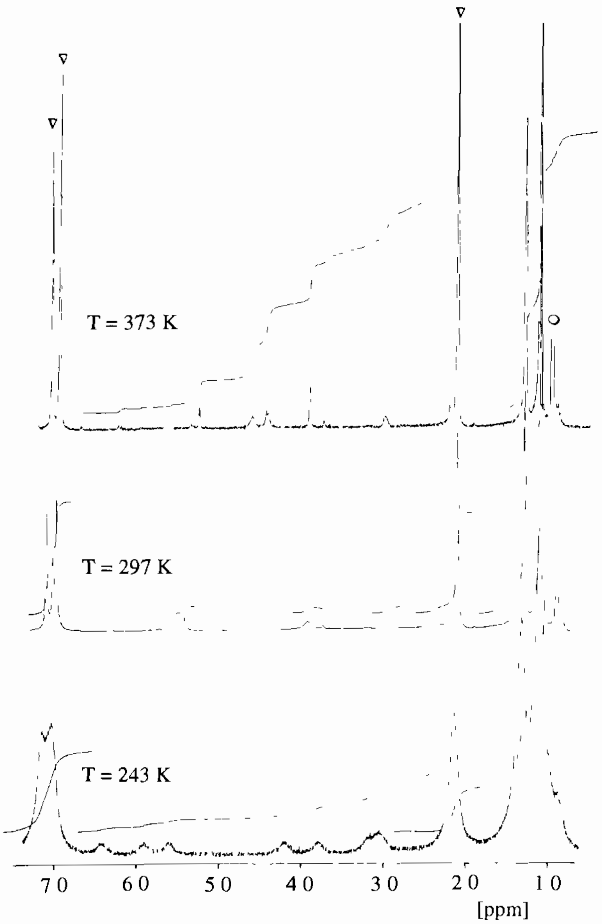


Fig. 2. Dynamic ^{1}H NMR spectra of **1**: ∇, C_7D_7H resonances; ○, PMe_3 containing products of thermal decomposition.

Dynamic ^{1}H NMR spectra

^{1}H NMR spectra of **1**–**3** were run at intervals of 20 K (**1**: 373–243 K, **2**: 297–193 K, **3**: 297–223 K) [22]. Thermal decomposition defined the upper limit and incipient crystallization of **3** causing line-broadening gave the lower limit.

Warming up **1** in toluene-d_8 revealed all eight azulene protons in a 1:2:2:2:1 pattern that is expected for η^5,η^5-coordination of azulene. Eight resonances were observed at 243 K representing the low-temperature limit that are consistent with η^5,η^3-coordination (Fig. 2). With olefinic H-7 and H-8 at lowest field and high-field H-4 and H-5 merging between 295 and 323 K one expects extreme broadening of these four resonances. The high field H-6 resonance is little affected but remains broad at all temperatures whereas H-2 at 373 K displays a 1:2:1 triplet pattern of the AB_2 spin system. H-1, H-3 resonances at 243 K are split by only 0.4 ppm and therefore remain distinct over the whole range. In the spectra of **2** and **3** signals at lowest field as in **1** are assigned to olefinic H-7 and H-8 in accord with their observed triplet and doublet pattern.

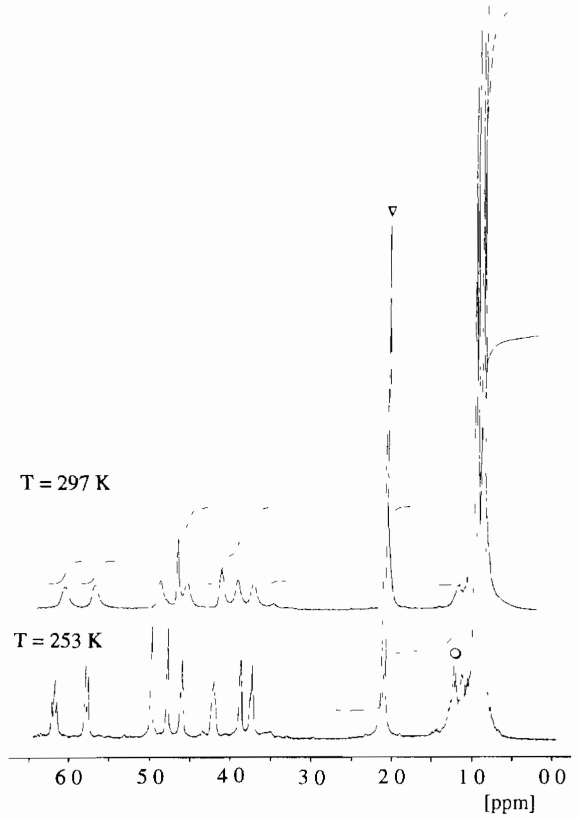


Fig. 3. Dynamic ^{1}H NMR spectra of **3**: ∇, C_7D_7H resonances; ○, PMe_3 containing products of thermal decomposition

As coupling of azulene protons is poorly resolved and the first-order criterion for analysis of this part of the spectrum is not satisfied, a full line-shape analysis was not attempted. However, all spectroscopic evidence is in accord with a fluxional π-allyl coordination of the $Co(PMe_3)_3$ group to two equivalent positions of the seven-membered azulene ring. A high-temperature limit is found at 100 °C for the site-exchange of **1**, while **2** and **3** (Fig. 3) barely show line-broadening at 20 °C and would decompose far below the fast exchange limit.

Estimates of the activation energies [18] are believed to be not very accurate due to the large range of proton shifts and arrive at about 15 kJ mol^{-1} for **1** and higher values for **2** and **3**.

Supplementary material

Complete lists of bond distances and angles including hydrogen atoms (Table 3), anisotropic parameters for non-hydrogen atoms (Table 4), and least-squares planes of the azulene ligand (Table 5) (9 pages), and a list of observed and calculated structure factors (Table 6) (13 pages) have been deposited with Fachinformationszentrum Energie Physik Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen, Germany as Supplementary Publication No. CSD 400634.

Acknowledgements

We thank the Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft for financial support of this work.

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