

Synthesis and crystal structure of new σ -bonded alkynylcobalt(III) complexes of 1,3-bis(diacetylmonoximeimino)propane

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Abstract

σ -Alkynyl Costa complexes can be readily synthesized from the *trans* diiodo-1,3-bis(diacetylmonoximeimino)propanecobalt complex **1** and alkynyl Grignard reagents **2a–d**. The conversions are carried out under daylight irradiation and give the cobalt acetylides **3a–d** in high yields. This photosubstitution method can be used to synthesize σ -alkynylcobalt(III) complexes with various substituents. The crystal structure of trimethylsilylethynyliodo-1,3-bis(diacetylmonoximeimino)propanecobalt(III) (**3a**) has been established by an X-ray diffraction study. The reaction of complexes **3a–d** with 4-*tert*-butylpyridine (**4**) in the presence of AgPF_6 gives positively charged complexes having the nitrogen base *trans* to the alkynyl ligand. Treatment of phenylethynyl-1,3-bis(diacetylmonoximeimino)propanecobalt(III) (**3b**) with I_2 gives quantitatively complex **1** and 1-iodo-2-phenylethyne (**6**).

Introduction

Until now only a few examples of vitamin B_{12} analogues containing a σ -bonded alkynyl were known, and they were limited to acetylene- and phenylacetylene derivatives of cobalamin [1] and related model compounds [2–4]. Other cobalt acetylides with six [5], four [6] or one [7,8] σ -bonded alkynyl ligands have been reported. The structures of these complexes are different from the others mentioned above since the cobalt is coordinated to non-corrinoid ligands.

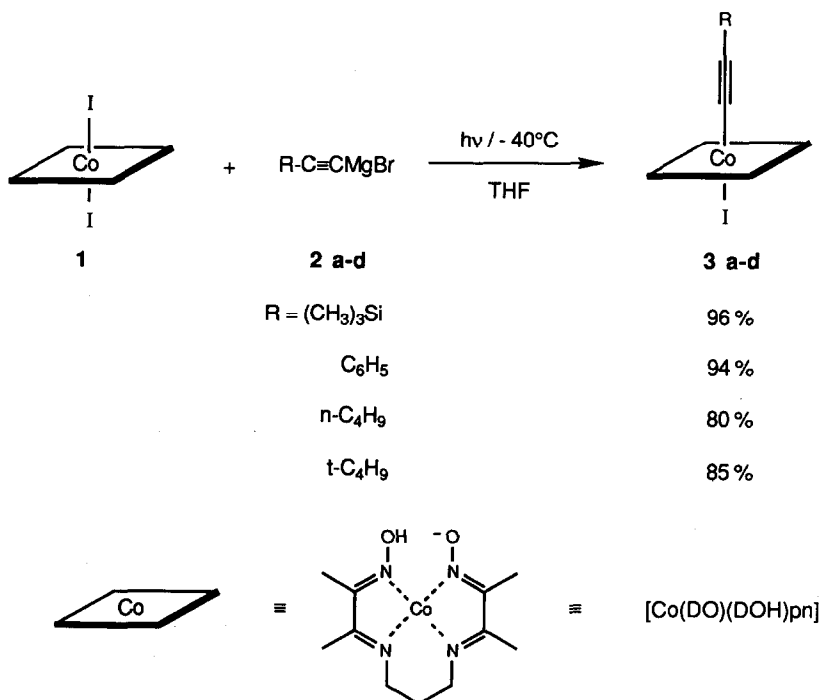
Although a number of alkyl Costa complexes have been known for a long time, no acetylide has previously been described [9–11]. σ -Alkynylcobalt(III) complexes of the type **3a–d** could be used as precursors for polymeric structures. In view of the existence of dialkyl Costa complexes [11] it could be concluded that diacetylides should be available. Such diacetylides or binuclear acetylides should act as appropriate building blocks for formation of organometallic polymers. Such polymeric structures could have interesting conductive properties [12,13].

Results and discussion

The reaction of alkyl Grignard reagents with the diiodo complex **1** gives the corresponding alkylcobalt(III) complexes [9]. However, simple treatment of **1** with the Grignard reagents **2a–d** did not give the expected σ -alkynyl complexes, but when **1** was allowed to react with the alkynyl Grignard reagents **2a–d** for 20–30 minutes under photolytic conditions at -40°C in THF the desired complexes **3a–d** were obtained (Scheme 1).

Irradiation with a daylight lamp is necessary to bring about this reaction, and either a photosubstitution or a photoredox reaction could lead to the observed products [14]. Hydrolysis and extraction with dichloromethane gives only a single product. The isolated complexes **3a–d** are brown to red-brown crystalline solids, stable in air, heat and light. The IR spectra in all cases display a sharp band at 2040 to 2120 cm^{-1} arising from the $\nu(\text{C}\equiv\text{C})$ vibration.

The ^1H NMR spectra in CDCl_3 show two singlets, at 2.34 to 2.37 ppm, assigned to the methyl protons of the equatorial ligand system. Peaks corresponding to the protons of the propano bridge are observed between 2.5 and 4.0 ppm. The signals from the protons of the substituent on the alkyne are not significantly shifted. In the ^{13}C spectra the signals of the alkynyl carbons β to cobalt are shifted downfield to between 98 and 108 ppm owing to the inductive effects of the fragment $[\text{Co}\{(\text{CO})(\text{COH})\text{pn}\}\text{I}]^+$. The signal from the alkynyl carbon α to cobalt is not observed owing to the long relaxation time for quaternary carbons and strong line



Scheme 1

Table 1

Spectroscopic data for **3a–d**

Compound	^{13}C NMR δ (ppm)		$\nu(\text{C}\equiv\text{C})$ (KBr) (cm^{-1})	λ_{max} (nm) (ϵ)
	$\beta\text{-C}$	$\gamma\text{-C}$		
3a	107.8		2040	360 (5470)
3b	100.5	127.2	2120	365 (6000)
3c	98.6	32.2	2110	362 (5540)
3d	107.5	28.6	2120	362 (5210)

broadening caused by the high quadrupole moment of the adjacent cobalt. Pertinent spectroscopic data are summarized in Table 1.

An X-ray diffraction study of complex **3a** was carried out. The geometry at the cobalt atom is that of a distorted octahedron. The cobalt is displaced out of the plane defined by four equatorial nitrogen atoms by 0.038 Å towards the acetylenic carbon atom. The iodine and the alkynyl group occupy the axial positions. The propano bridge is bent out of the equatorial plane in direction of the alkynyl group (Fig. 1). The angle between the two planes is about 67°.

X-ray studies on related cobalt complexes bearing axial carbon ligands have revealed a cobalt–carbon bond length of 1.99 Å in methylaquo Costa complex [15] and 1.97 Å in cyanocobalamin [16,17]. The Co–C(1) bond length in complex **3a** is 1.948(5) Å. These shorter bond lengths in the cobalamin and alkynylcobalt complexes are presumably due to the different effects of sp^3 and sp hybridisation.

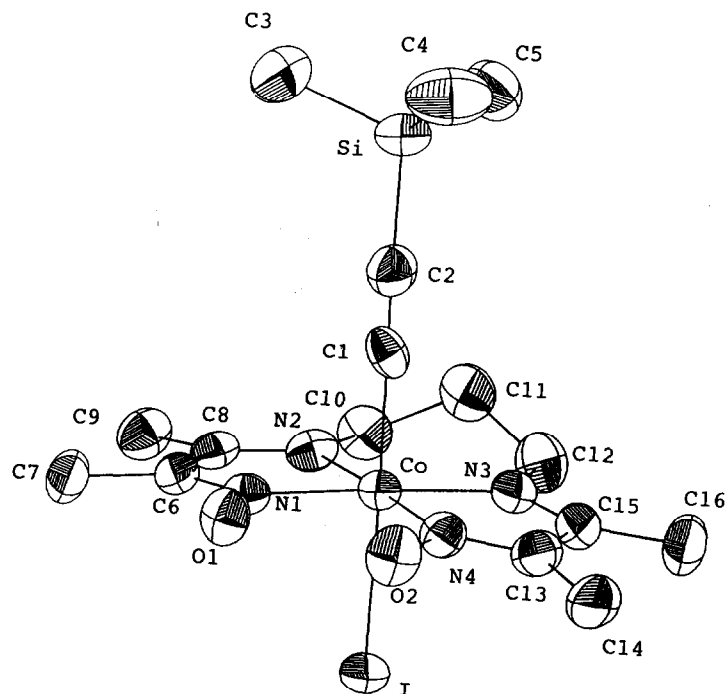
Fig. 1. ORTEP-drawing and numbering scheme of compound **3a**.

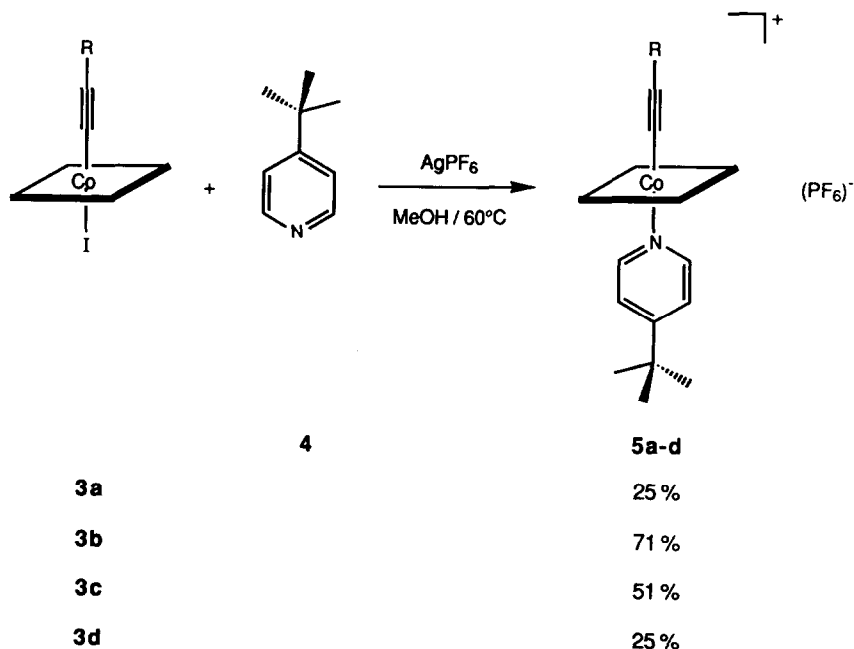
Table 2

Selected bond lengths (Å) and angles (°) for $[(\text{CH}_3)_3\text{SiC}\equiv\text{C})\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}\text{I}]$, **3a**

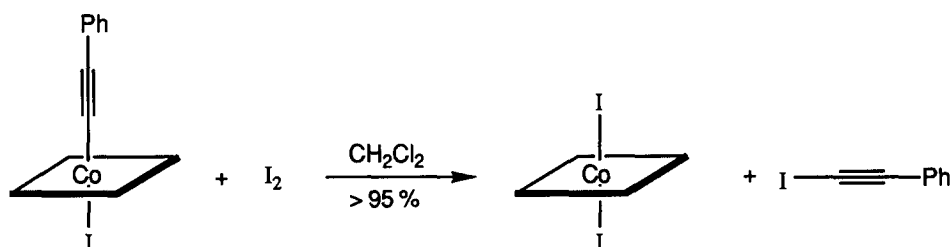
Co–C(1)	1.948(5)	Co–C(1)–C(2)	175.3(5)
Co–N(1)	1.896(4)	C(1)–C(2)–Si	173.0(5)
Co–N(2)	1.906(4)	I–Co–C(1)	177.8(1)
Co–I	2.634(1)	N(1)–Co–N(2)	81.6(2)
C(1)–C(2)	1.127(7)	N(2)–Co–N(3)	99.5(2)
C(2)–Si	1.851(6)	N(4)–Co–N(1)	97.4(2)

The C(1)–C(2) triple bond in complex **3a** is 1.127(7) Å long. It is very short compared with that in free acetylene. All other bond lengths and angles are similar to those of the corresponding methylaquo derivative [15]. The O(1) ... O(2) distance, 2.44 Å, is in the range of values found for related Co complexes [18]. The hydrogen atom of the intramolecular –O ... H ... O– hydrogen bond could not be located crystallographically but it is detected in the ^1H NMR spectra as a sharp singlet at 18 to 20 ppm. Deviations from an ideal 180° bonding angle at the termini of the alkynyl moiety are caused by intermolecular interactions in the crystal packing. π -Back bonding would be expected to result in elongation of the triple bond, but since the alkynyl C–C bond length is 1.127(7) Å such back bonding must be absent (Table 2).

Complexes **3a–d** can easily be transformed into positively charged species **5a–d** by ligand substitution with a nitrogen base (Scheme 2). The replacement of iodide by 4-tert-butylpyridine (**4**) occurred in the presence of AgPF_6 . The base **4** and the



Scheme 2



Scheme 3

complex anion PF_6^- increase the solubility of the complexes **5a–d** in organic solvents such as chloroform, dichloromethane, acetone, methanol and ethanol. The pyridine complexes **5a–d** are light yellow, and are air- and light-stable.

The Co–C bond is cleaved in the presence of iodine by electrophilic attack on the alkynyl ligand (Scheme 3), as expected for organometallic complexes [19]. Iodonolysis gives quantitatively the diiodo complex **1** and 1-iodo-2-phenylethyne (**6**).

Concluding remarks

Complexes **3a–d** and **5a–d** are to our knowledge the first examples of σ -alkynylcobalt(III) complexes containing the 1,3-bis(diacetylmonoximeimino)propane ligand. These complexes can be isolated in high yields as brown to red-brown solids, stable to light, air and heat. Slight modification of the ligand *trans* to the alkynyl moiety should lead to more reactive species. The possibility of using these complexes as building blocks for novel organocobalt polymers is being examined.

Experimental

Reactions were carried out under dry argon. THF was degassed and purified by distillation under argon from benzophenone radical anion. Diiodo-1,3-bis(diacetylmonoximeimino)propanecobalt(III) was synthesized by the procedure of Costa [9]. Alkynyl Grignard reagents were prepared as previously described [20]. All other reagents were purchased and used as supplied. Flash chromatography was performed on silica gel C 560KV 35–70 μm (Chemische Fabrik Uetikon).

¹H NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer in deuteriochloroform with 0.05% TMS as an internal standard. ¹³C NMR were recorded on a Varian Gemini spectrometer at 75.5 MHz. IR spectra were recorded on a Perkin Elmer 981 spectrophotometer as KBr pellets. Mass spectra were obtained with a Varian MAT 212 spectrometer. UV/Vis spectra were recorded on a Hewlett Packard HP 8450 spectrophotometer.

All irradiations were carried out with an Osram Power Star HQI/T 250D (250 W) daylight lamp.

*General procedure for the preparation of [(RC≡C)Co{(DO)(DOH)pn}I], **3a–d***

A solution of 15 mmol of the alkynyl Grignard reagent in 20 ml of THF was added at -40°C to a solution of diiodo-1,3-bis(diacetylmonoximeimino)propane-

cobalt(III) (**1**) (5 mmol) in 200 ml of THF, the mixture being irradiated for 30 minutes during the addition. The colour of the solution changed from dark-green to orange-brown. The mixture was stirred for 20 minutes at -40°C and then poured into 100 ml of ice water. Three extractions with 100 ml portions of dichloromethane was followed by drying of the extracts over MgSO_4 and evaporation under reduced pressure. The residue was purified by flash chromatography (dichloromethane/acetone/ethyl acetate 6:3:1). The crystals were dried under reduced pressure at room temperature.

$[(\text{CH}_3)_3\text{SiC}\equiv\text{C})\text{Co}\{(\text{CO})(\text{COH})\text{pn}\}\text{I}]$ (**3a**) (96%), as red crystals; m.p. = 185°C (decomp.); ^1H NMR (CDCl_3): δ -0.11 (s, 9H), 2.34 (s, 6H), 2.36 (s, 6H), 2.51–2.58 (m, 2H), 3.84–4.09 (m, 4H); ^{13}C NMR (CDCl_3): δ 0.91, 13.11, 17.01, 28.19, 107.78, 153.69, 170.84; IR (KBr) = 2040 cm^{-1} $\nu(\text{C}\equiv\text{C})$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , $\text{cm}^2\text{ m}^{-1}$)): 464 (430), 360 sh (5470), 286 (28340); mass spectrum (FAB): m/e (relative intensity) 523 ($M+1$, 2.9%), 425 ($M-\text{C}_5\text{H}_9\text{Si}$, 11%), 395 ($M-1.52\%$), 298 ($M-\text{I}-\text{C}_5\text{H}_9\text{Si}$, 100%); anal. found: H, 5.67; C, 37.55; N, 10.80. $\text{C}_{16}\text{H}_{28}\text{CoI}_2\text{N}_4\text{O}_2\text{Si}$ calc.: H, 5.41; C, 37.79; N, 10.73%.

$[(\text{PhC}\equiv\text{C})\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}\text{I}]$ (**3b**) (95%), as brown crystals; m.p. = 183°C (decomp.); ^1H NMR (CDCl_3): δ 2.35 (s, 6H), 2.38 (s, 6H), 2.57–2.62 (m, 2H), 3.95–4.11 (m, 4H), 7.04–7.14 (m, 5H); ^{13}C NMR (CDCl_3): δ 13.16, 17.05, 49.83, 100.53, 125.70, 127.16, 127.80, 131.63, 153.87, 171.02; IR (KBr) = 2120 cm^{-1} $\nu(\text{C}\equiv\text{C})$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , $\text{cm}^2\text{ m}^{-1}$)): 474 (380), 365 (6000), 283 (36840), 278 (38690); mass spectrum (FAB): m/e (relative intensity) 527 ($M+H$, 6.8%), 425 ($M-\text{C}_8\text{H}_5$, 3.7%), 399 ($M-\text{I}$, 24.4%), 298 ($M-\text{I}-\text{C}_8\text{H}_5$, 100%); anal. found: H, 4.81; C, 43.20; N, 10.58; $\text{C}_{19}\text{H}_{24}\text{CoI}_2\text{N}_4\text{O}_2$ calc.: H, 4.60; C, 43.36; N, 10.65%.

$[(n\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}\text{I}]$ (**3c**) (80%), as red-brown crystals; m.p. = 185°C (decomp.); ^1H NMR (CDCl_3): δ 0.80 (t, J 6.7 Hz, 3H), 1.17–1.24 (m, 4H), 2.04 (t, J 6.7 Hz, 2H), 2.34 (s, 6H), 2.37 (s, 6H), 2.52–2.59 (m, 2H), 3.75–4.14 (m, 4H); ^{13}C NMR (CDCl_3): δ 13.06, 13.39, 16.88, 20.31, 21.19, 28.31, 32.25, 49.75, 67.91, 98.63, 153.52, 170.53; IR (KBr) = 2110 cm^{-1} $\nu(\text{C}\equiv\text{C})$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , $\text{cm}^2\text{ m}^{-1}$)): 474 (400), 362 (5540), 282 (26500); mass spectrum (FAB): m/e (relative intensity) 507 ($M+H$, 9.4%), 425 ($M-\text{C}_6\text{H}_9$, 8.4%), 379 ($M-\text{I}$, 42.2%), 298 ($M-\text{I}-\text{C}_6\text{H}_9$, 100%); anal. found: H, 5.18; C, 40.43; N, 10.95; $\text{C}_{17}\text{H}_{28}\text{CoI}_2\text{N}_4\text{O}_2$ calc.: H, 5.57; C, 40.33; N, 11.07%.

$[(t\text{-C}_4\text{H}_9\text{C}\equiv\text{C})\text{Co}\{(\text{DO})(\text{DOH})\text{pn}\}\text{I}]$ (**3d**) (85%), as light brown crystals; m.p. = 150°C (decomp.); ^1H NMR (CDCl_3): δ 0.95 (s, 9H), 2.33 (s, 6H), 2.37 (s, 6H), 2.54–2.59 (m, 2H), 3.82–4.14 (m, 4H); ^{13}C NMR (CDCl_3): δ 13.03, 16.85, 28.24, 28.61, 32.26, 49.66, 107.54, 153.27, 170.28; IR (KBr) = 2120 cm^{-1} $\nu(\text{C}\equiv\text{C})$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , $\text{cm}^2\text{ m}^{-1}$)): 474 (430), 362 (5210), 282 (23930); mass spectrum (FAB): m/e (relative intensity) 507 ($M+H$, 3%), 425 ($M-\text{C}_6\text{H}_9$, 7%), 379 ($M-\text{I}$, 47.4%), 298 ($M-\text{I}-\text{C}_6\text{H}_9$, 100%); anal. found: H, 5.31; C, 40.33; N, 10.77; $\text{C}_{17}\text{H}_{28}\text{CoI}_2\text{N}_4\text{O}_2$ calc.: H, 5.57; C, 40.33; N, 11.07%.

Preparation of complexes **5a–d**

To a solution of 200 mg of **3a–d** in a minimum of methanol were added 1.1 equivalents of 4-tert-butylpyridine (**4**). The solution was warmed to 40°C and 1 equivalent of AgPF_6 was added, the colour of the solution changing immediately from dark-brown to orange. After filtration of the warm solution the solvent was

removed under reduced pressure. Addition of 70 ml of pentane/diethyl ether (1:1) to the oil caused the separation of a yellow solid, which was filtered off and dissolved in dichloromethane/acetone/ethyl acetate (6:3:1). After adsorptive filtration the solution was evaporated under reduced pressure and light yellow crystals were obtained. Recrystallisation from acetone/pentane gave the complexes **5a–d**.

$[(CH_3)_3SiC\equiv C]Co\{(DO)(DOH)pn\}(4\text{-tert-bupy})] (PF_6) (\mathbf{5a})$ (25%), as yellow crystals; m.p. = 191°C (decomp.); 1H NMR ($CDCl_3$): δ -0.04 (s, 9H), 1.27 (s, 9H), 2.11–2.19 (m, 1H), 2.39 (s, 6H), 2.49 (s, 6H), 2.62–2.86 (m, 1H), 3.91–4.16 (m, 4H), 7.50 (d, J 6.7 Hz, 2H), 7.70 (d, J 6.7 Hz, 2H), 18.61 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 1.0, 13.28, 17.75, 27.56, 29.93, 35.03, 49.51, 110.24, 124.26, 148.22, 154.76, 164.33, 174.91; IR (KBr) = 2060 cm^{-1} $\nu(C\equiv C)$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , cm^2 mM^{-1})): 520 (30), 310 (2750), 237 (12820); mass spectrum (FAB): m/e (relative intensity) 530 ($M^+ - PF_6$, 100%), 395 ($M^+ - PF_6 - 4\text{-tert-bupy}$, 18%), 298 ($M^+ - PF_6 - 4\text{-tert-bupy} - C_7H_5Si$, 41%); anal. found: H, 6.17; C, 44.74; N, 10.33; $C_{25}H_{41}CoF_6N_5O_2PSi$ calc.: H, 6.12; C, 44.44; N, 10.36%.

$[(PhC\equiv C)Co\{(DO)(DOH)pn\}(4\text{-tert-bupy})] (PF_6) (\mathbf{5b})$ (71%), as light yellow crystals; m.p. = 202°C (decomp.); 1H NMR ($CDCl_3$): δ 1.27 (s, 9H), 2.42 (s, 6H), 2.52 (s, 6H), 2.64 (m, 2H), 4.04 (m, 4H), 7.14 (m, 5H), 7.55 (d, J 6.6 Hz, 2H), 7.77 (d, J 6.6 Hz, 2H), 18.73 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 13.09, 17.58, 27.51, 29.76, 34.87, 49.54, 101.78, 124.51, 126.99, 131.66, 148.31, 155.46, 164.63, 175.84; IR (KBr) = 2110 cm^{-1} $\nu(C\equiv C)$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , cm^2 mM^{-1})): 654 (10), 314 (5280), 257 (40330); mass spectrum (FAB): m/e (relative intensity) 534 ($M^+ - PF_6$, 100%), 399 ($M^+ - PF_6 - 4\text{-tert-bupy}$, 18%), 298 ($M^+ - PF_6 - 4\text{-tert-bupy} - C_8H_5$, 41%); anal. found: H, 5.68; C, 49.76; N, 10.15; $C_{28}H_{37}CoF_6N_5O_2P$ calc.: H, 5.49; C, 49.51; N, 10.31%.

$[(n-C_4H_9C\equiv C)Co\{(DO)(DOH)pn\}(4\text{-tert-bupy})] (PF_6) (\mathbf{5c})$ (51%), as yellow crystals; m.p. = 186°C (decomp.); 1H NMR ($CDCl_3$): δ 0.83 (t, J 7.1 Hz, 3H), 1.18–1.29 (m, 9H + 4H), 2.05–2.11 (m, 2H + 1H), 2.39 (s, 6H), 2.48 (s, 6H), 2.60–2.64 (m, 1H), 3.90–4.10 (m, 4H), 7.49 (d, J 6.7 Hz, 2H), 7.74 (d, J 6.7 Hz, 2H), 18.69 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 13.25, 13.60, 17.67, 20.43, 21.51, 29.99, 32.23, 35.05, 49.63, 100.17, 124.24, 148.19, 154.72, 164.20, 174.76; IR (KBr) = 2140 cm^{-1} $\nu(C\equiv C)$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , cm^2 mM^{-1})): 469 (300), 305 (5320), 232 (24330); mass spectrum (FAB): m/e (relative intensity) 514 ($M^+ - PF_6$, 100%), 379 ($M^+ - PF_6 - 4\text{-tert-bupy}$, 43%), 298 ($M^+ - PF_6 - 4\text{-tert-bupy} - C_8H_9$, 65%); anal. found: H, 6.28; C, 47.64; N, 10.50; $C_{26}H_{41}CoF_6N_5O_2P$ calc.: H, 6.26; C, 47.35 N, 10.62%.

$[(t-C_4H_9C\equiv C)Co\{(DO)(DOH)pn\}(4\text{-tert-bupy})] (PF_6) (\mathbf{5d})$ (25%), as yellow crystals; m.p. = 197°C (decomp.); 1H NMR ($CDCl_3$): δ 0.98 (s, 9H), 1.26 (s, 9H), 1.96–2.01 (m, 1H), 2.39 (s, 6H), 2.48 (s, 6H), 2.56–2.61 (m, 1H), 3.86–4.07 (m, 4H), 7.49 (d, J 6.4 Hz, 2H), 7.70 (d, J 6.4 Hz, 2H), 18.65 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 13.23, 17.68, 27.54, 28.96, 30.02, 32.36, 35.05, 49.60, 109.26, 124.21, 148.13, 154.66, 164.14, 174.76; IR (KBr) = 2120 cm^{-1} $\nu(C\equiv C)$; UV/Vis (CH_2Cl_2): λ_{max} (nm (ϵ , cm^2 mM^{-1})): 458 (220), 306 (4580), 257 sh (7560), 264 sh (10000), 239 (20590), 234 (20580); mass spectrum (FAB): m/e (relative intensity) 514 ($M^+ - PF_6$, 100%), 379 ($M^+ - PF_6 - 4\text{-tert-bupy}$, 43%), 298 ($M^+ - PF_6 - 4\text{-tert-bupy} - C_8H_9$, 65%); anal. found: H, 6.28; C, 47.64; N, 10.50; $C_{26}H_{41}CoF_6N_5O_2P$ calc.: H, 6.26; C, 47.35 N, 10.62%.

X-ray analysis of 3a: Crystal data

Compound **3a** ($\text{C}_{16}\text{H}_{28}\text{CoIN}_4\text{O}_2\text{Si}$), $M = 522.35$, monoclinic, $a = 7.892(5)$, $b = 25.928(6)$, $c = 11.112(5)$ Å, $\beta = 102.88(1)^\circ$, $U = 2216.5(3)$ Å³ (by least-squares refinement of diffractometer angles for 25 automatically centered reflections, $\lambda = 0.71069$ Å), space group $P2_1/n$ (non-standard no. 14), $Z = 4$, $D_c = 1.565$ g cm⁻³, $F(000) = 1048$. Red crystals mounted in a 0.3 mm Lindemann capillary tube under nitrogen, $\mu(\text{Mo-K}\alpha) = 20.98$ cm⁻¹. Intensity data were collected on a Enraf–Nonius CAD4-diffractometer, $\omega/2\theta$ -scan, graphite monochromated Mo- $K\alpha$ radiation; 4750 independent reflections measured, $[(\pm h, +k, +l); 2 < \theta < 28^\circ]$. 4224 reflections with $F > 2\sigma(F)$. No correction for absorbance was applied. The structure was solved by the Patterson method and refined by conventional difference Fourier and full matrix least-squares methods, using the program SHELX-76 [21]. The weighting scheme was $1.38/(\sigma(F^2) + 2.433 \times 10^{-3}F^2)$. Non hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated and included in the final calculations with U_{iso} fixed at 0.06. The final residuals were $R = 0.049$, $R_w = 0.054$. Table 3 shows atomic fractional coordinates.

A complete list of bond lengths and angles and lists of observed and calculated structure factors are available from the authors.

Table 3

Coordinates and equivalent thermal parameters of **3a** with estimated standard deviations in parenthesis

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^a
Co	0.13038(8)	0.14508(2)	0.03294(5)	2.71
C1	0.1952(6)	0.1170(2)	-0.1131(5)	3.03
C2	0.2243(7)	0.1029(2)	-0.2023(5)	4.12
Si	0.2484(2)	0.0843(1)	-0.3584(1)	4.11
C3	0.0281(10)	0.0830(3)	-0.4627(7)	5.48
C4	0.3818(12)	0.1325(4)	-0.4177(7)	7.42
C5	0.3507(13)	0.0199(3)	-0.3599(8)	7.40
I	0.04244(5)	0.18652(1)	0.22667(3)	3.94
N1	0.3527(5)	0.1763(2)	0.0784(4)	2.97
O1	0.4901(4)	0.1521(2)	0.1469(3)	3.91
C6	0.3676(6)	0.2223(2)	0.0411(4)	3.21
C7	0.5331(7)	0.2536(2)	0.0725(5)	3.97
C8	0.2030(6)	0.2424(2)	-0.0323(4)	3.07
C9	0.1888(8)	0.2976(2)	-0.0745(5)	4.21
N2	0.0752(5)	0.2093(2)	-0.0500(4)	3.18
C10	-0.1002(7)	0.2222(2)	-0.1167(5)	4.01
C11	-0.2012(7)	0.1758(3)	-0.1737(5)	4.28
C12	-0.2500(7)	0.1376(3)	-0.0857(6)	4.61
N3	-0.0958(5)	0.1132(2)	-0.0062(4)	3.42
C13	0.0592(8)	0.0518(2)	0.1266(5)	4.06
C14	0.0819(10)	0.0051(2)	0.2077(6)	5.27
C15	-0.1063(7)	0.0700(2)	0.0491(5)	4.01
C16	-0.2725(8)	0.0407(3)	0.0438(7)	5.33
N4	0.1861(5)	0.0833(2)	0.1223(4)	3.35
O2	0.3452(5)	0.0730(2)	0.1879(4)	4.28

^a $B_{\text{eq}} = (8/3)\pi^2(U_{11} + U_{22} + U_{33})$

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References

- 1 G.C. Hayward, H.A.O. Hill, J.M. Pratt, N.J. Vanston and R.J.P. Williams, *J. Chem. Soc.*, (1965) 6485.
- 2 G.N. Schrauzer and J. Kohnle, *Chem. Ber.*, 97 (1964) 3056.
- 3 G. Mestroni, G. Zassinovich, A. Camus and G. Costa, *J. Organomet. Chem.*, 92 (1975) C35.
- 4 D. Cummins, E.D. McKennzie and A. Segnitz, *J. Organomet. Chem.*, 87 (1975) C19.
- 5 R. Nast, *Coord. Chem. Rev.*, 47 (1982) 89.
- 6 E. Rojas, A. Santos, V. Moreno and C. del Pinto, *J. Organomet. Chem.*, 181 (1979) 365.
- 7 A.M. Van den Bergen, R.L. Elliot, C.J. Lyons, K.P. Mackinnon and B.O. West, *J. Organomet. Chem.*, 297 (1985) 361.
- 8 R. Kergoat, P. L'Harridon, L.C. Gomes de Lima, C. Jegat, N. Le Berre, M.M. Kubiki and J.E. Guerchais, *J. Organomet. Chem.*, 389 (1990) 71.
- 9 G. Costa, G. Mestroni and E. de Savorgnani, *Inorg. Chim. Acta*, 3 (1969) 323.
- 10 G. Costa, G. Mestroni, G. Tausher and L. Stefani, *J. Organomet. Chem.*, 6 (1966) 181.
- 11 G. Costa and G. Mestroni, *J. Organomet. Chem.*, 11 (1968) 325.
- 12 A. Wong, P.C.W. Kang, C.D. Tagge and D.R. Leon, *Organometallics*, 8 (1990) 1992.
- 13 J.E. Sheets, C.E. Caraher, Jr. and C.U. Pittman, Jr. (Eds.) *Metal-Containing Polymeric Systems*, Plenum, New York, NY, 1985.
- 14 V. Balzani, L. Moggi and V. Carassiti, *Ber. Bunsenges, Phys. Chem.*, 72 (1968) 288.
- 15 S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 3 (1969) 278.
- 16 C. Brink, V. Schomaker, D.W. Cruickshank, D.G. Hodgkin, M.J. Kamper and D. Pilling, *Proc. R. Soc., A* 278 (1964) 1.
- 17 D.G. Hodgkin, J. Lindsey, R.A. Sparks, K.N. Trueblood and J.C. White, *Proc. R. Soc., A* 266 (1962) 494.
- 18 N. Bresciani-Pahor, M. Forcolin, L.G. Marzilli, L. Randaccio, M.F. Summers and P.J. Toscano, *Coord. Chem. Rev.*, 63 (1985).
- 19 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, in *Principles and Application of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
- 20 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1971.
- 21 G. Sheldrick, *SHELX-76*, University of Göttingen, Germany.