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Dicobalt hexacarbonyl-3-butyn-1-yl cobaloxime: synthesis X-ray crystal structure and reactions of the first combined cobaloxime–dicobalt hexacarbonyl alkyne complex

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Abstract

Reaction of 1-butynyl cobaloxime (**1**), synthesised by displacement of the corresponding tosylate with cobaloximato nucleophile, with dicobalt octacarbonyl gives the first trimetallic cobaloxime–dicobalt hexacarbonyl-alkyne complex (**2**). This trimetallic species is characterised by X-ray crystallography and undergoes the Pauson-Khand reaction to give cobaloxime-substituted cyclopentenones. We believe these are the first examples of Pauson-Khand reactions of alkynes which contain a carbon-to-metal sigma bond.
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Keywords: Cobaloxime; Cobalt carbonyl; Trimetallic complex; Pauson-Khand; Multinuclear complex

1. Introduction

Metal alkyne and alkynyl [1a] complexes including dicobalt hexacarbonyl–alkyne [1b] complexes are of interest due to both their many potentially useful properties and applications [1a,2] and their applications in synthetic chemistry, notably the Pauson-Khand reaction [3] and the Nicholas reaction [4] in which a Lewis acid removes an oxy-group from the propargyl position of a dicobalt hexacarbonyl alkyne complex to give a cobalt-stabilised cation, which can then be trapped with nucleophiles (Scheme 1). Often in synthesis this reaction is followed by oxidative demetallation of the alkyne to give overall propargylic substitution of oxy-alkynes. Also of interest are alkyl cobaloximes, which have been used as model systems for the carbon–cobalt bond of coenzyme vitamin B12 [5], as catalysts in living radical polymerisation [6] and in synthetic chemistry [7] due to both their properties as radical precursors [7b] and their ability to stabilise carbocations as the cobaloximato π cation (Scheme 2) [7c]. Very recently, new interest in cobaloxime chemistry has been generated by the ability of both B12 and cobaloximes to dehalogenate priority pollutants such as tetrachloroethene [7d].

Although multinuclear systems are of great current interest [8], no system has yet been reported in which these two very different classes of organocobalt species are combined in the same molecule and this paper reports the first studies of such compounds. It is possible that combined cobaloxime–dicobalt hexacarbonyl systems could provide useful routes to cyclic organometallics via the Pauson-Khand reaction, or that cations stabilised by both cobalt-containing units could be isolated or applied as synthetic intermediates. We were particularly intrigued as to whether these functional groups could be connected via a sigma-bonded framework with the alkynyl functionality, and hence the dicobalt hexacarbonyl complex, pendant from the cobaloxime cobalt, as opposed to through the axial pyridine ligand in the cobaloxime unit. The various activating effects of the cobaloxime group and the dicobalt hexacarbonyl would thus be acting upon the same portion of a methylene chain, and this may either lead to useful reactivity or instability of the complexes.

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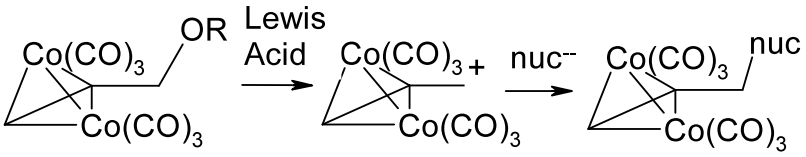
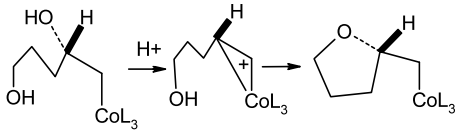


Scheme 1.



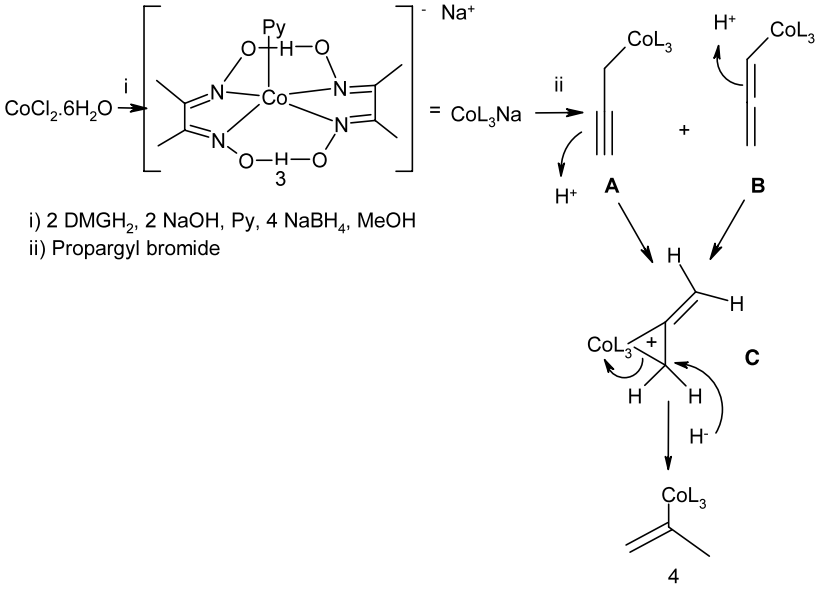
Scheme 2.

Two possible approaches to these combined systems are available: the displacement of a leaving group from a preformed dicobalt hexacarbonyl complex, and the treatment of an alkynyl cobaloxime with dicobalt octacarbonyl. As it is known that treatment of dicobalt hexacarbonyl complexes with organometallic nucleophiles can displace cobalt from the complex [8c], the latter approach was chosen.

2. Results and discussion

2.1. Synthesis and characterisation

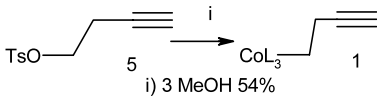
Treatment of propargyl bromide with the cobaloximato-nucleophile (**3**) prepared under standard conditions [9] gave not the expected propargyl cobaloxime **A**, nor the allene **B** which might be expected from an S_N2' mechanism, but a product which we have tentatively assigned as 2-propenylcobaloxime (**4**) (Scheme 3). Although single crystals suitable for X-ray diffraction have not been obtained, NMR and MS indicate that this is the correct structure as the mass of 410 and the proton and carbon NMR indicates reduction of the alkyne to an alkene. Additionally, DEPT confirms the presence of a methyl group indicating reduction of the propargyl unit. It is not obvious how this material is formed and it differs from the literature precedent in which propargyl chlorides are reported to give mixtures of the propargyl and allenyl products [10]. The reduction of the propargyl unit to give alkenyl products is explicable by the use of sodium borohydride in the synthesis of the cobaloximato nucleophiles, and it seemed possible that excess borohydride reduces one of the expected products **A** or **B** which, along with reduction, rearranges to give a 2-cobaltopropene system. Although the standard conditions [9] for alkylation of cobaloximes which were followed in this work include the addition of a second portion of borohydride after the cobaloximato-nucleophile has been treated with alkyl halide, and this step is an obvious culprit for over-reduction, omission of this second addition, in fact, led to higher yields of **4**. In order to probe the mechanism of formation of this unexpected product, a reaction was performed between the cobaloximato nucleophile and propargyl bromide under standard conditions but with the addition of excess acetone 15 min after the addition of propargyl bromide, in order to destroy excess borohydride, quench



Scheme 3.

any reductive rearrangements, and allow the isolation of intermediates **A** or **B**. Two products which were tentatively assigned as **A** and **B** were indeed observed in the crude ^{1}H-NMR of the products of these reactions. In addition to the signals assigned to pyridine and DMGH units, the characteristic signals which allowed assignment as **A** are a doublet of integration 2H at δ 3.9 ppm and a triplet of integration 1H at δ 2.2 ppm with a mutual coupling of 2.5 Hz, typical of a propargyl system, similarly **B** was assigned on the basis of a doublet of integration 2H at δ 5.4 ppm and a triplet of integration 1H at δ 4.8 ppm with a mutual coupling of 5.9 Hz, typical of a mono-substituted allene. Although this crude product was a reasonably clean mixture of these two species, each of them appeared to be unstable even in the absence of reductant, and attempts to isolate either of these putative intermediates failed. Although mechanistic studies are ongoing, a tentative proposal for the formation of **4** is illustrated in Scheme 3. In this, both **A** and **B** are converted a common intermediate cobaloxime π cation **C** by protonation of the π system by the medium, which in each case involves migration of cobalt, mirroring the mechanisms precedented in Scheme 2 [7c,9]. This intermediate **C** is then reduced by borohydride with addition of hydride at the least substituted carbon to give **4**.

Given the lack of success with propargyl bromide, attention was turned to the homopropargyl system. Treatment of but-3-yn-1-ol tosylate (**5**) [11] with the sodium cobaloximato nucleophile prepared under standard conditions [9] gave the required but-3-yn-1-ylcobaloxime (**1**) in a reasonable yield (Scheme 4). The air and water stability of these organometallics is highlighted by the fact that crystals suitable for X-ray diffraction were grown from a methanol–water mixture under ambient atmosphere. To the best of our knowledge, this is the first crystallographically characterised alkyne-containing cobaloxime, although such species have been invoked previously. The NMR of this and subsequent cobaloximes show signals corresponding to the methylene unit directly attached to cobalt in the ^{1}H-NMR in the typical methylene envelope (in this case δH = 1.56); however, the interpretation of ^{13}C-NMR is complicated by broadening of the signal corresponding to the carbon directly attached to the cobalt atom. In many cases, this signal is difficult to observe and appears as such a weak broad signal that it can only be confidently assigned by the use of ^{1}H–^{13}C correlation. This broadening is presumably a result of coupling to the highly quadrupolar ^{59}Co nucleus; however, no



Scheme 4.

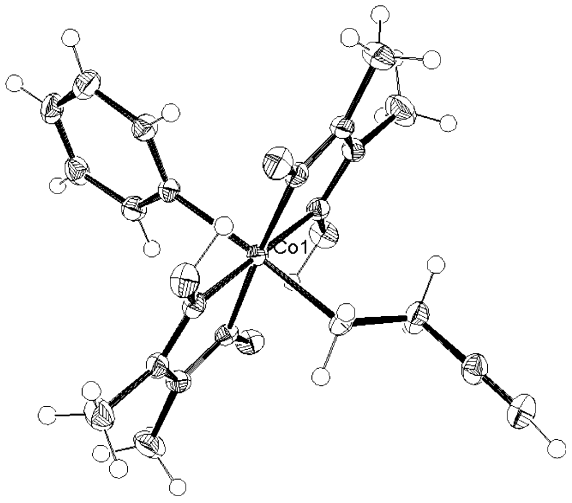
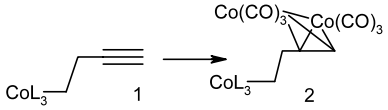


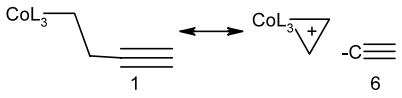
Fig. 1. ORTEP view of But-3-yn-1-ylcobaloxime 1.

significant broadening of the signals attributed to the protons attached to these carbons is observed (see Fig. 1).

It might have been expected that the stability of a cobaloxime π cation [7,9] and of the alkynyl anion would lead to a lengthening of the methylene to quaternary C–C bond (Scheme 6), but in fact this length is 1.477 Å compared to 1.470 Å 12 to 1.475 Å [13] in some of the few examples of crystallographically characterised hex-1-ynes (in which the cobalt of **1** is replaced by a methylene unit) indicating that this putative resonance form **6** makes little if no contribution. But-3-yn-1-yl cobaloxime (**1**) is stable to moderate heat (decomposition occurs under prolonged heating greater than 80 °C), air and water, but is slowly degraded in bright light. Treatment of **1** with dicobalt octacarbonyl in toluene or DCM (degassed) leads to the immediate formation of a deep red solution and the evolution of a gas (assumed to be carbon monoxide) (Scheme 5). NMR of the product obtained upon pumping down these solutions indicate that the dicobalt hexacarbonyl alkyne complex has formed as the alkyne proton (δ 1.87 ppm $CDCl_3$) disappears and is replaced by a broad signal at δ 5.88 ppm ($CDCl_3$) characteristic of the complex. The reaction is essentially quantitative; however, the crude product is always contaminated by a small amount of black insoluble material assumed to be metallic cobalt which can be removed by filtration of a toluene solution, followed by precipitation of the product as very dark red to black crystals (68%) with 60–80% petroleum ether (see Fig. 2).



Scheme 5.



Scheme 6.

Again, this tricobalt organometallic species is reasonably stable to air and water, seeming to be oxidised slowly in solution but, again, it could be crystallised from aqueous alcoholic solution providing that oxygen was excluded. Crystallisation from toluene/60–80% petroleum ether gave single crystals of dicobalt hexacarbonyl–but-3-yn-1-yl cobaloxime which were suitable for X-ray diffraction studies. Again, all bond lengths (C–C, C–Co, Co–Co) are consistent with the small number [14] of examples of acyclic dicobalt hexacarbonyl–but-1-ynyl complexes which have been crystallographically characterised indicating that there is no significant contribution from a π cobaloxime cation.

2.2. Reactions

Having established that the two forms of cobalt–carbon species are compatible and can exist in the same molecule (indeed show remarkable stability), it was of interest to see if the reactivity of the dicobalt hexacarbonyl unit was retained in the presence of cobaloxime substitution. The substrate in hand was considered suitable for a Pauson-Khand [3] reaction and indeed this proceeded cleanly with strained bicyclic alkenes in moderate yields (Scheme 7). These yields compare disfavourably with the literature equivalents for metal-free systems, but in many cases these reactions are not strictly comparable as NMO [3c] or a similar atom-transfer oxidant has been used to promote the Pauson-Khand reaction, and attempts to promote the Pauson-Khand reactions of **1** with NMO lead to the formation of a mixture of demetallated products, demonstrating the limit to which the cobaloxime unit may be exposed to oxidants. The Pauson-Khand may also be thermally promoted; however, heating alkyl cobaloximes homolyses the cobalt–carbon bond and an attempt to run the reaction at 100 °C in toluene led to decomposition to an intractable black tar. Cobaloxime homolysis is an effective method for initialising alkene polymerisation, and it is likely that the alkyne–alkene mixture which represents the Pauson-Khand reaction is highly sensitive to the alkyl-cobaloxime/alkyl radical couple generated from these species at high temperature. The yields represent the optimum result of a range of temperature/solvent combinations which were investigated, and the balance between driving the Pauson-Khand reaction to completion and formation of by-products was best at reflux in dichloromethane. Although the yields are thus lower than idea, they represent an unpromoted Pauson-Khand reaction of an alkyne–dicobalthexacarbonyl complex which is relatively stable and thus may be expected to react sluggishly.

The complex tricyclic products of the Pauson-Khand reactions were studied by 1D and 2D NMR and all the peaks unambiguously assigned by application of gCOSY, HSQC, HMBC and NOSY spectroscopy. Generally, the assignment of spectral peaks of cobaloximes may be complicated by difficulties in observing the carbon (and occasionally its attached hydrogens) directly attached to cobalt due to quadrupolar broadening from ^{59}Co.

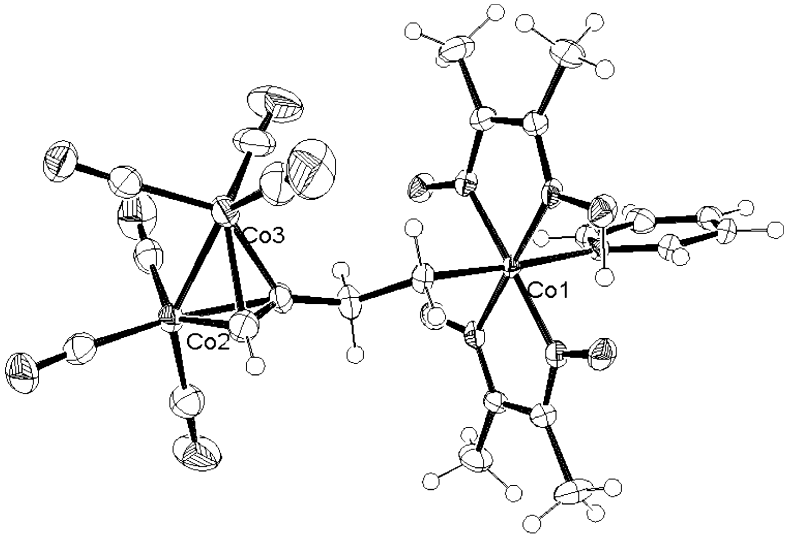
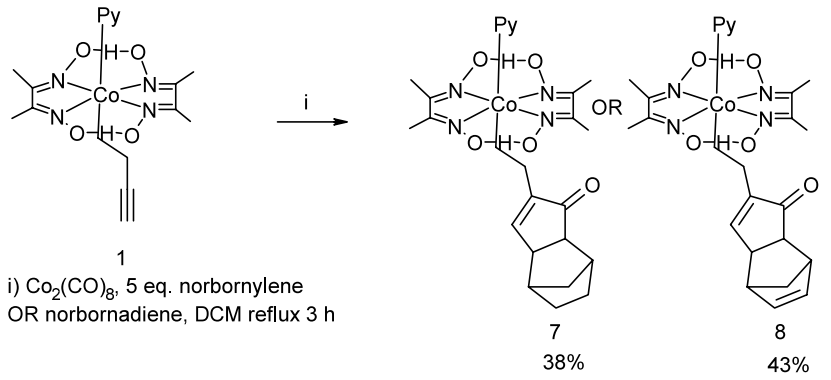


Fig. 2. ORTEP view of dicobalt hexacarbonyl but-3-yn-1-ylcobaloxime 2.



Scheme 7.

3. Conclusion

In conclusion, the first combined cobaloxime–dicobalt hexacarbonyl alkyne complex has been prepared, and it has been shown that these remarkably stable organotrimetallics retain the synthetically useful chemistry associated with the Pauson-Khand reaction to give organometallic products. Studies are ongoing into reducing the cobaloxime to alkyne connectivity and into other sigma-bonded organometallic species suitable for use in the Pauson-Khand reaction.

4. Experimental

4.1. Crystal data

Crystallographic data for compounds **1** and **2** have been given in Tables 1 and 2, respectively.

4.1.1. General

NMR spectra were recorded on a Bruker DPX 400 MHz at 399.9 MHz (proton) and 100.0 MHz (carbon) and on an INOVA-500 MHz at 499.9 MHz (proton) and 125.7 MHz (carbon). Unless otherwise stated NMR spectra were recorded in $CDCl_3$. IR spectra were recorded on a Perkin–Elmer 1600 FT-IR: mass spectra were recorded on a VG Fisons Platform II or at the EPSRC national mass spectrometry service in Swansea (HRMS). Unless otherwise specified, all chemicals and reagents were commercial materials used without further purification. Solvents for reactions involving dicobalt octacarbonyl were dried with molecular sieves and degassed by three freeze–pump–thaw cycles prior to use. Exposure of cobaloximes to light was minimised where possible. A satisfactory analysis of **4** was never obtained. Although **4** could be crystallised from methanol to give material which was pure by NMR, this homogeneity was rapidly lost and unidentified decomposition products appeared. Similarly, homoallyl cobaloximes **7** and **8** are less stable than their alkynyl precursor **1**.

Table 1
Crystal data and experimental details for **1**, orange block, stable under ambient conditions collected on a Nonius KappaCCD solved using direct methods [15]

Formula	$C_{17}H_{24}CoN_5O_4$
Molecular weight	421
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2(1)/C$
λ (Å)	0.71073
Unit cell dimensions	
a (Å)	9.104(2)
b (Å)	14.491(3)
c (Å)	14.516(3)
α (°)	90
β (°)	90.60(3)
γ (°)	90
V (Å^3)	1908.9(7)
Z	4
Absorption coefficient (mm^{-1})	0.932
Crystal size (mm^3)	$0.2 \times 0.2 \times 0.2$
θ Limits (°)	3.08–27.52
Reflections collected	25112
Unique observed reflections [$F_o > 4\sigma F_o$]	4367
R_{int}	0.0980
Goodness-of-fit on F^2	1.110
Final R indices [$I > 2\sigma(I)$]	
R_1	0.0428
$wR_2(F)^2$	0.1052
All data	
R_1	0.0580
$wR_2(F)^2$	0.1118

4.1.2. But-3-yn-1 p-toluenesulphonate (5) [11]

To DCM (260 ml) at 0 °C was added triethylamine (11.2 ml, 80 mmol), then 3-butyn-1-ol (3.9 ml, 50 mmol). *p*-TosCl (10.7 g, 55 mmol) was added as a solid in portions during a period of 5 min. The reaction was stirred at ambient temperature for 60 h and then quenched with ice water (30 ml). The organic layer was separated and treated with aqueous hydrochloric

Table 2
Crystal data and experimental details for **2**, dark red needle, stable under ambient conditions, collected on Nonius KappaCCD solved using direct methods [15]

Formula	$C_{23}H_{24}Co_3N_5O_{10}$
Molecular weight	707
Temperature (K)	150
Crystal system	triclinic
Space group	$P\bar{1}$
λ (Å)	0.71073
Unit cell dimensions	
a (Å)	8.9732(2)
b (Å)	11.2696(3)
c (Å)	15.4905
α (°)	69.5420(10)
β (°)	76.8790(10)
γ (°)	84.090(2)
V (Å^3)	1428.87(7)
Z	2
Absorption coefficient (mm^{-1})	1.782
Crystal size (mm^3)	0.2 × 0.1 × 0.05
θ Limits (°)	2.98 26.00
Reflections collected	23589
Unique observed reflections [$F_o > 4\sigma F_o$]	5562
R_{int}	0.0844
Goodness-of-fit on F^2	1.104
Final R indices [$I > 2\sigma(I)$]	
R_1	0.0539
$wR_2(F)^2$	0.1412
All data	
R_1	0.0672
$wR_2(F)^2$	0.1544

acid (1 M, 30 ml), sodium bicarbonate (30 ml) and with brine (30 ml), then dried over magnesium sulphate and evaporated to give the 3-butyn-1-o-tosylate (**4**) as a pale yellow liquid (11.2 g, 87.5%) of sufficient purity to be used in further steps. δH = 7.73 (d, J = 8.0 Hz, 2H, Ar–H2,6), 7.3 (d, J = 8.0 Hz, 2H, Ar–H3,5), 4.03 (t, J = 7.0 Hz, 2H, CH_2CH_2O), 2.49 (dt, J = 7.0 and 2.7 Hz, CH_2CH_2O), 2.38 (s, 3H, CH_3), 1.91 (t, J = 2.7 Hz, 1H, HCC) ppm [11].

4.1.3. Prop-1-enyl-2-cobaloxime (*4*)

All work was done under dry nitrogen and with degassed solvent. Cobalt(II) chloride hexahydrate (0.96 g, 4.03 mmol), dimethylglyoxime (0.92 g, 7.92 mmol), aqueous NaOH (50%, 0.585 g, 14.63 mmol) and pyridine (0.34 ml, 4.2 mmol) were added successively each in one portion to MeOH (22 ml). The mixture was deoxygenated for 10 min by bubbling N_2 and then cooled to 0 °C. Sodium borohydride (0.215 g, 5.68 mmol) was added in two aliquots within 1 min and the mixture stirred for 10 min. Progargyl bromide (80% solution in toluene, 0.45 ml, 4.2 mmol) was added via syringe in one portion and the mixture was stirred for 2 h while it attained ambient temperature. Additional sodium borohydride (0.067 g, 1.77 mmol) was added in one portion and the mixture was stirred for one more hour. The reaction mixture was adsorbed onto silica (2 g). This brown powder was put on top of a plug of fresh silica (20 g). This was rinsed with petroleum ether (200 ml) and with ethyl acetate (500 ml) to give an orange solution. Evaporation and crystallisation from methanol gave an orange powder (0.2 g, 12%) (Rf 0.16 ether) (**4**). m.p. 180 °C (decomp.) δH = 8.57 (dd, J = 1.4 and 6.4 Hz, 2H, pyr–H2,6) 7.67 (m, 1H, pyr–H4), 7.28 (m, 2H, pyr–H3,5), 4.55 (s, 1H, HHC=C), 4.21 (s, 1H, HHC=C), 2.04 (s, 12H, 4 × DMGH CH_3), 1.55 (s, 3H, CH_3) ppm; δC = 150.3, 150.1 (both N=C, DMGH, pyr–C2,6), 138.0 (pyr–C4), 126.3 (very weak, C–Co(CH_3)), 125.3 (pyr–C3,5), 115.5 (H_2CC), 29.6 (CH_3), 13.6 (DMGH CH_3) ppm. DEPT confirms assignments as CH, CH_3; m/z (ES) 410 [M + H$^+$], ν_{max}(Nujol) = 3407 (broad, weak) 2865, 1558, 1237 cm^{-1}.

4.1.4. But-3-yn-1-yl cobaloxime (*1*)

Cobalt(II) chloride hexahydrate (0.96 g, 4.03 mmol), dimethylglyoxime (0.92 g, 7.92 mmol), aqueous NaOH (50%, 0.585 g, 14.63 mmol) and pyridine (0.34 ml, 4.2 mmol) were each added successively in one portion to MeOH (22 ml). The mixture was deoxygenated for 10 min by bubbling N_2 and then cooled to 0 °C. Sodium borohydride (0.215 g, 5.68 mmol) was added in two aliquots within 1 min and the mixture stirred for 10 min. **5** (0.94 g, 4.2 mmol) was added and the mixture was stirred for 3 h at 0 °C. The reaction mixture was adsorbed onto silica (3.5 g). This brown powder was put on top of a plug of fresh silica (35 g). This was washed with petroleum ether (100 ml), petroleum ether/ethyl acetate (1:1) (500 ml) and with ethyl acetate (500 ml) to give an orange solution. Evaporation of the ethyl acetate portion followed by crystallisation from methanol (40 ml MeOH per 1 g raw product) gave an orange powder (Rf 0.45 EtOAc) (0.918 g, 54%) (**1**). m.p. 225–230 °C (decomp), δH = 8.49 (dd, J = 1.3 and 6.1 Hz, 2H, pyr–H2,6), 7.67 (m, 1H, pyr–H4), 7.26 (m, 2H, pyr–H3,5), 2.06 (s, 12H, 4 × CH_3 DMGH), 1.87 (t, J = 2.5 Hz, 1H, HC≡C), 1.71 (dt, J = 2.5 and 8.7 Hz, 2H, $HCCCH_2$), 1.56 (t, J = 8.7 Hz, 2H, CH_2Co) ppm; δC = 150.3 (MeC=N, ligand), 150.1 (pyr–C2,6), 138.0 (pyr–C4), 125.7 (pyr–C3,5), 85.3 (HCC), 67.3 (HC≡C), 27.5 (weak, broad, CH_2Co), 18.9 (propargy CH_2), 12.5 (CH_3, DMGH) ppm; assignments CH, CH_2, CH_3 confirmed by DEPT other than δ 27.5 ppm (weak, broad, CH_2Co), which was not observed by DEPT, assignment of this peak was confirmed by ^{13}C–^{1}H correlation to the methylene signal at δH 1.56 ppm, ν_{max}(Nujol) = 3236, 2086 (weak), 1558, 1227 cm^{-1}; m/z (ES) 422 [M + H$^+$]; $C_{17}H_{24}N_5O_4Co$ requires C, 48.46; H, 5.74; N, 16.62; Found: C, 48.33; H, 5.72; N, 16.55%.

4.1.5. But-3-yn-1-yl cobaloxime dicobalt hexacarbonyl (2)

To a solution of **1** (125 mg, 0.3 mmol) in dry, degassed toluene (10 ml) was added dicobalt octacarbonyl (105 mg, 0.3 mmol) as a solid in one portion. The mixture was stirred under nitrogen for 3 h during which time cobalt carbonyl dissolved, evolution of carbon monoxide ceased and the solution turned a deep red colour. Evaporation followed by crystallisation (toluene/60–80% petroleum ether) gave red-black needles (144 mg, 68%) (**2**) m.p. $>300\ ^{\circ}C$. $\delta H = 8.53$ (d, $J = 4.9$ Hz, 2H, pyr–H2,6), 7.66 (m, 1H, pyr–H4), 7.26 (m, 2H, pyr–H3,5), 5.88 (br s, 1H, H_4), 2.4 (t, $J = 7.9$ Hz, 2H, H2), 2.07 (s, 12H, 4 × DMGH CH_3), 1.59 (t, $J = 7.9$ Hz, 2H, H_1) ppm; δC (CD_3CN) 198.5 (very broad, weak CO), 149.1, 148.7 (DMGH C=N, Py–C2,6), 137.2 (Py–C3,5), 134.0 (Py–C4), 32.5 (weak, CH_2Co), 10.2 (CH_2CH_2Co) ppm; *m/z* (FAB) 708 [M+H], 629 [M+H−pyr], 573 [M+H−pyr−2CO], 545 [M+H−pyr−3CO]; ν_{max}(Nujol) = 3410 (broad weak), 2855, 2081, 2031, 1980 1558 1227 cm^{-1}; $C_{23}H_{24}N_5O_{10}Co_3$ requires C, 39.06; H, 3.42; N, 9.90; Found: C, 39.33; H, 3.37; N, 9.71%.

4.1.6. Tricyclo[4.3.1^{2,5}]-8-en-8-ethylcobaloxim-7-decanone

7 (0.5 g, 1.19 mmol) was dissolved in DCM to which dicobalt octacarbonyl (0.44 g, 1.29 mmol) was added in one portion and the solution was stirred for 30 min during which time evolution of carbon monoxide ceased and a deep red colour developed. Norbornylene (0.51 mg, 5.43 mmol) was added in one portion and the reaction mixture was heated to reflux for 3 h. The reaction mixture was adsorbed onto 2.5 g of silica. Column chromatography (35 g of silica, petrol ether/ethyl acetate (1:3), then ethyl acetate) gave a brown powder (Rf 0.3 EtOAc) (**7**) (245 mg, 38%). $\delta H = 8.58$ (d, $J = 5.0$ Hz, 2H, H1), 7.73 (t, $J = 7.5$ Hz, 1H, H3), 7.32 (m, 2H, H2), 7.04 (s, 1H, H16), 2.45 (s, 1H, H15), 2.30 (s, 1H, H11), 2.14 (s, 12H, H5), 2.09 (m, 2H, H14, H10), 1.73 (m, 2H, H7), 1.61 (m, 4H, 2 × H6, H12exo, H13exo), 1.23 (m, 2H, H12endo, H13endo), 0.96 (d, $J = 9.3$ Hz, 1H, H17a), 0.88 (d, $J = 9.3$ Hz, 1H, H17b) ppm; $\delta C = 210.6$ (C9), 157.9 (C16), 149.8 (C1), 149.4, 149.3 (C4, C8), 137.4 (C3), 152.1 (C2), 53.6 (C10), 48.0 (C15), 38.8 (C11), 37.9 (C14), 31.0 (C17), 29.0 (C12), 28.4 (C13), 27.4 (broad, weak C6), 24.7 (C7), 12.0 (C5) ppm; *m/z* (ES) = 544 [M+H$^+$]; ν_{max}(Nujol) = 2855, 1689, 1558, 1232 cm^{-1}. Crystallisation from MeOH/H_2O gave brown powder. $C_{25}H_{38}CoN_5O_6$ ($M \cdot 2H_2O$) requires C, 53.28; H, 6.79; N, 12.43; Found: C, 52.97; H, 6.25; N 12.22%.

Assignments were arrived at from 1H–1H correlation working from uniquely identifiable ^1H H16, methylene $6CH_2$ (identified by HSQC correlation with broad ^{13}C signal showing adjacent ^{59}Co C6) and ^{13}C C9 identified by typical and distinct δ value 210. gCOSY, HSQC and HMBC from these signals allowed assignment of 6-17, H12,13, end/exo differentiated by ^{1}Hendo, NOESY to H15 and H13exo NOESY to H14. H17a and H17b distinguished by stronger correlation in gCOSY between H17a and H12,13endo, attributed to W-like relationship (see Fig. 3).

4.1.7. Tricyclo[4.3.1^{2,5}]-8-en-8-ethylcobaloxim-7-decanone (8)

1 (0.5 g, 1.19 mmol) was dissolved in DCM to which dicobalt octacarbonyl (0.44 g, 1.29 mmol) was added in one portion and the solution was stirred for 30 min during which time evolution of carbon monoxide ceased and a deep red colour developed. Norbornadiene (0.6 ml, 5.54 mmol) was then added in one portion and the reaction mixture was heated to reflux for 3 h. The reaction mixture was adsorbed onto 2.5 g of silica. Column chromatography (35 g of silica, petrol ether/ethyl acetate (1:3), then ethyl acetate) gave a brown powder (Rf 0.33 EtOAc) (**8**) (278 mg, 43%). $\delta H = 8.55$ (d, $J = 5.0$ Hz, 2H, H1), 7.68 (t, $J = 7.6$ Hz, 1H, H2), 7.31 (m, 2H, H3), 7.03 (s, 1H, H16), 6.16 (m, 1H, H13), 6.08 (m, 1H, H12), 2.80 (s, 1H, H11), 2.52 (s, 2H, H14,15), 2.07 (s, 13H, 12 × H5+H10), 1.68 (m, 2H, H7), 1.54 (m, 2H, H6), 1.23 (d, $J = 9.2$ Hz, 1H, H17b), 1.09 (d, $J = 9.2$ 1H, 17a) ppm; $\delta C = 209.3$ (C9), 157.9 (C16), 150.8 (C8), 149.8 (C4), 149.4 (C1), 138.3 (C3), 137.4 (C13), 136.9 (C12), 125.1 (C2), 52.3 (C10), 47.4 (C15), 43.4 (C11), 42.8 (C14), 41.2 (C17), 26.5 (broad, weak C6), 25.0 (C7), 12.0 (C5) ppm; ν_{max}(Nujol) = 3467 (broad weak), 2855, 1694, 1599, 1558 cm^{-1}; *m/z* (ES) 542 [M+H$^+$]. Crystallisation from MeOH/H_2O gave a brown powder. m.p. 119–121 °C. $C_{25}H_{34}CoN_5O_5$ ($M \cdot H_2O$) requires C, 55.25; H, 6.31; N, 12.89; Found: C, 54.95; H, 6.31; N, 12.72%.

Assignments arrived at from 1H–1H correlation working from uniquely identifiable 1H H16 and distinct pair H12,13 with pairs H12,13 H11,14 H 10,15 differentiated by NOESY and gCOSY correlations between H16 H15 and H13. H17a and H17b distinguished by stronger correlation in gCOSY between H17b and H15, H10, attributed to W-like relationship (see Fig. 4).

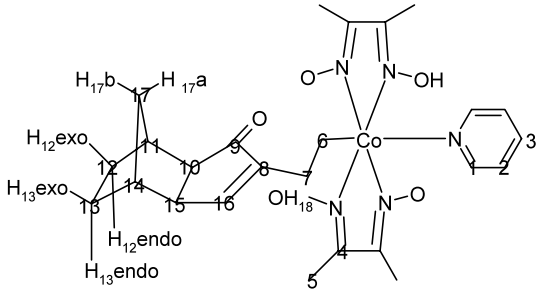


Fig. 3. Numbering for tricyclo[4.3.1^{2,5}]-8-en-8-ethylcobaloxim-7-decanone.

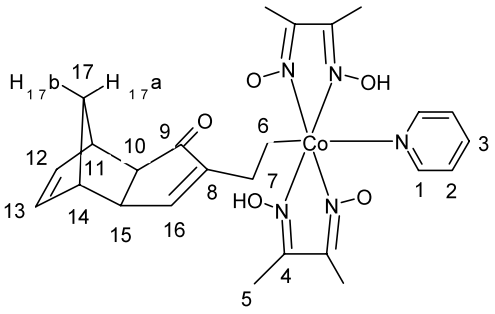


Fig. 4. Numbering for tricyclo[4.3.1^{2,5}]-8-en-8-ethylcobaloxim-7-decanone.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallography Data Centre, CCDC No. 194766 for compound **1** and CCDC No. 194765 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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