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Synthesis and characterization of cobalt and molybdenum complexes derived from linear conjugated diynenes, triynedienes and tetraynetrienes

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Abstract

Z-1,6-Bis(trimethylsilyl)hexa-1,5-diyn-3-ene (**2a**), *E*-hexa-1,5-diyn-3-ene (**3b**) and related compounds (**3a**, **c** and **d**) were synthesized by standard methods. The Grignard reagent (**3e**) derived from 1-phenylhexa-1,5-diyn-3-ene (**3d**) was coupled with *E*-1-chloro-4-phenyl-1-buten-3-yne to give *E*,*E*-1,10-diphenyldeca-1,5,9-triyne-3,7-diene (**4**) and with *E*-1,2-dichloroethene to give *E*,*E*,*E*-1,14-diphenyltetradeca-1,5,9,13-tetrayne-3,7,11-triene (**5**). Hexa-1,5-diyn-3-ene complexes coordinated to one (**7a**, **8**) and two (**6a–d**) hexacarbonyldicobalt units were prepared from the appropriate ligands and octacarbonyldicobalt. Tris- (**9**) and tetrakis- (**10**) hexacarbonyldicobalt complexes of the triynediene (**4**) and tetraynetriene (**5**) ligands were prepared similarly. Mono (**7b**) and bis (**6e**) di-η^5-cyclopentadienyltetracarbonyldimolybdenum complexes of *E*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene were prepared by treating free diynene (**3a**) with the appropriate amount of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$. Spectroscopic characteristics (NMR, IR, UV) of the complexes are presented and discussed.

Introduction

There is current interest in materials containing highly conjugated organic [1] and organometallic frameworks [2]. The discovery of third order optical nonlinearity in soluble polydiacetylenes (**1**) [3,4] encouraged us to study such effects in metal-containing analogues, including η-bonded species [5]. It was realized that spectroscopic characterization of such polymers would be aided by comparison with model η-bonded organometallics related to the conjugated framework of polydiacetylenes. Examples of such models include complexes derived from enynes with extended conjugation or from cumulated butatrienes. In this paper, we describe the synthesis and characterization of cobalt and molybdenum η^2-complexes with linear conjugated diynene, triynediene and tetraynetriene ligands.

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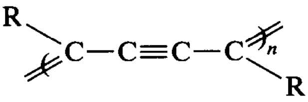

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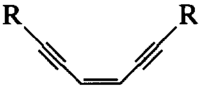


(2)

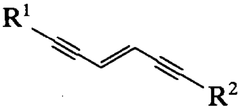
(a) R = $SiMe_3$

(b) R = Ph

Results and discussion

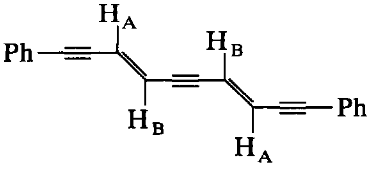
Synthesis of ligands

Ligands were synthesized by established transition metal-mediated Grignard coupling reactions. *Z*-1,6-Disubstituted hexa-1,5-diyne-3-enes (**2a,b**) and the *E*-analogue (**3a**) have been previously reported [6,7]; the unsymmetrically substituted diynene (**3c**) was prepared by [$NiCl_2$(dppp)]-promoted coupling of trimethylsilylacetylene magnesium bromide [6] and *E*-1-chloro-4-phenyl-1-buten-3-yne [8].



(3) R^1	R^2
(**a**) $SiMe_3$	$SiMe_3$
(**b**) H	H
(**c**) Ph	$SiMe_3$
(**d**) Ph	H
(**e**) Ph	MgBr

Desilylation reactions of **3a** and **3c** were effected by lithium hydroxide in aqueous tetrahydrofuran [9] to give the previously reported parent diynene **3b** [6] and the new compound **3d**, respectively. The latter (**3b, d**) are unstable at room temperature, and were stored in n-pentane solution at *ca.* −25 and −5°C, respectively, prior to complexation. The monosubstituted hexa-1,5-diyne-3-ene (**3d**) was transformed with ethyl magnesium bromide into a Grignard reagent (**3e**) which was coupled separately with *E*-1-chloro-4-phenyl-1-buten-3-yne and *E*-1,2-dichloroethene to give the previously unreported compounds, triynediene (**4**) and tetraynetriene (**5**), in 13 and 10% yields, respectively.



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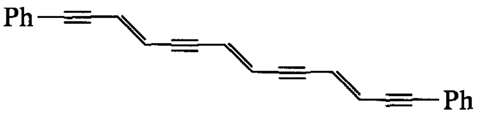
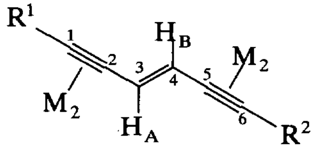
Synthesis of complexes

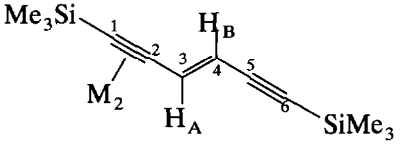
Bis-hexacarbonyldicobalt complexes (**6a–d**) of *E*-hexa-1,5-diyne-3-ene derivatives (**3a–d**) were obtained in good yields by treating 1 molar equiv. of the ligand with 2 molar equiv. of octacarbonyldicobalt. The products were stable solids (for **6a–c**); the complex **6d** was a labile black oil which was characterized spectroscopically, but which could not be obtained analytically pure. A notable feature of the present work is isolation of a stable complex **6b** from the labile ligand, *E*-hexa-1,5-diyne-3-ene (**3b**). It is likely that the ligand could be oxidatively regenerated from the complex in a process that could offer a convenient, ready source of the diynene for synthetic use [10]. It proved more difficult to prepare pure samples of mono-hexacarbonyldicobalt complexes with *E*-hexa-1,5-diyne-3-ene ligands. For example, reaction of **3a** with 1 molar equiv. of octacarbonyldicobalt gave a complex product, from which the mono-ligated species **7a** was obtained as a labile red oil; the latter was characterized spectroscopically, but could not be obtained analytically pure. Treatment of *Z*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene (**2a**) with two molar equiv. of octacarbonyldicobalt under conditions that had been used for the transformation **3a** → **6a** gave only a monohexacarbonyldicobalt complex **8**, with much unreacted octacarbonyldicobalt. The reluctance of the *Z*-ligand **2a** to form a bis-dicobalt-hexacarbonyl complex (*cf.* **6a**) can be ascribed to steric hindrance; *cf.* analogous complexes relating to the chemistry of *Esperamicin A* [11].



(**5**)



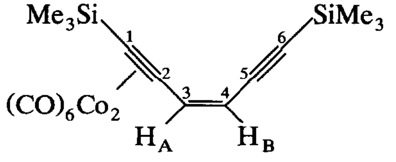
(**6**) R^1	R^2	M$_2$
(**a**) SiMe$_3$	SiMe$_3$	$Co_2(CO)_6$
(**b**) H	H	$Co_2(CO)_6$
(**c**) Ph	SiMe$_3$	$Co_2(CO)_6$
(**d**) Ph	H	$Co_2(CO)_6$
(**e**) SiMe$_3$	SiMe$_3$	$Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$



(**7**)

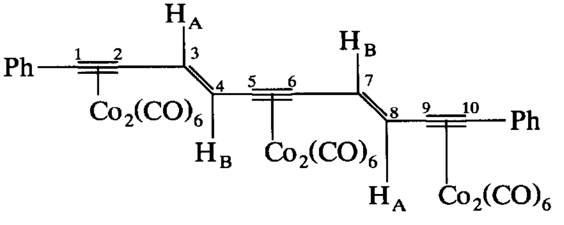
(**a**) $M_2 = Co_2(CO)_6$

(**b**) $M_2 = Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$



(**8**)

The enyne derivatives with extended conjugation (**4** and **5**) were successfully converted into solid, fully-metallated, tris- (**9**) and tetrakis- (**10**) hexacarbonyldicobalt complexes, respectively, but no attempts were made to isolate pure specimens of incompletely metallated compounds that contained free alkyne moieties.



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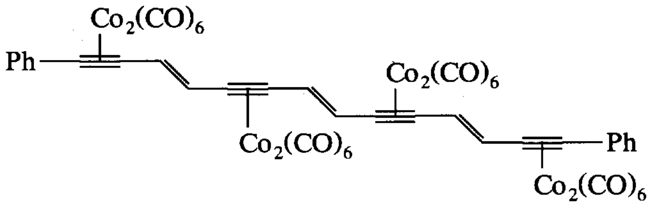

(10)

A bis(di-η^5-cyclopentadienyltetracarbonyldimolybdenum) complex (**6e**) of the *E*-hexa-1,5-diyn-3-ene ligand (**3a**) was prepared in good yield by treating the diynene with 2 molar equiv. of di-η^5-cyclopentadienyltetracarbonyldimolybdenum [12]. In contrast, use of an equimolar amount of the latter reagent gave a complex product from which the mono-ligated compound **7b** could be isolated in low yield (19%).

Spectroscopic properties of complexes

Comparison of selected ^1H and ^{13}C NMR spectral data of complexes and free ynenes (listed in the Experimental section) serves to highlight a number of trends. The ^1H resonance of an alkene-hydrogen adjacent to a metal-complexed alkyne function in diynene, triynediene or tetraynetriene (*e.g.* H_A in **6** and **7**) is shifted to higher frequency by *ca.* 1 ppm, compared to its chemical shift in the free ligand, whereas an alkene-hydrogen remote from a coordination site (*e.g.* H_B in **7a** or **7b**) is little shifted on metallation. Similar chemical shift patterns have been noted in hexacarbonyldicobalt complexes involved in chemistry of relevance to *Esperamicin A* [11]. The marked high frequency shift in resonance of a terminal H-atom attached to an alkyne coordinated by $Co_2(CO)_6$ relative to its chemical shift in the free alkyne, observed for $[Co_2(C_2H_2)(CO)_6]$ (*i.e.* from δ 1.8 to 5.82 ppm) [13], is also apparent for **6b** (δ 4.35 to 6.36 ppm) and **6d** (δ 3.2 to 6.37 ppm).

The ^{13}C resonances of alkyne C-atoms are shifted on complexation by $Co_2(CO)_6$ or $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, but with chemical shifts encompassing a range from *ca.* 20 ppm lower to *ca.* 6 ppm higher in frequency than the free ynene, depending on the nature of the group attached terminally to the alkyne bond. Metal coordination to an alkyne bond is clearly shown by a high frequency shift of > 10 ppm in the ^{13}C NMR for resonance of the adjacent, conjugated alkene C-atom; in the fully metallated complexes with longer conjugated chains, **9** or **10**, all alkene C-atoms, although structurally inequivalent, are observed at identical chemical shifts and this contrasts with the same C-atoms in the free ligands which show the expected 2 or 3 resonances, respectively, separated over 2 ppm. This observation might suggest that the ligated alkyne moiety is the dominant factor influencing the chemical shift of the adjacent alkene C-atoms. In the unsymmetrical, mono-ligated complexes, **7a** and **7b**, the alkene C-atom adjacent to the coordinated alkyne system (C-3) experiences a large high frequency shift (18–26 ppm) whereas the other alkene C-atom (C-4) adjacent to the free alkyne bond, resonates at a significantly lower frequency than in the free ligand (8–14 ppm); a similar chemical shift pattern has been reported for hexacarbonyldicobalt [14] and dicyclopentadienyltetracarbonyldimolybdenum [15] complexes of simple 1,3-enynes. This shift difference between the two alkene-C atoms is in line with the reactivity of related systems, the more shielded C-4 centre being susceptible to attack by electrophiles and C-3 readily forming a cationic centre. The ^{13}C resonance of the *ipso*-C atom of a terminal phenyl group bonded to a metallated alkyne unit is also shifted by *ca.* 16 ppm to higher frequency than in an uncoordinated molecule.

Infrared spectra of all hexacarbonyldicobalt complexes in hexane solution show six $\nu(CO)$ bands, including a weak band around 1980 cm^{-1}, consistent with the presence of tetrahedrane units $Co_2(C_2RR')(CO)_6$ [16]. The di-η^5-cyclopentadienyltetracarbonyldimolybdenum complexes **6e** and **7b** show four $\nu(CO)$ bands in their solution IR spectra, including a band at 1835 or 1855 cm^{-1}, respectively, assignable to a semi-bridging carbonyl group, as observed in reported Mo_2C_2 tetrahedrane complexes $[Mo_2(C_2RR')(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [17].

The free ynene compounds **3**–**5** display UV spectra with lowest energy electronic transitions at λ_{max} 286–388 nm ($\epsilon > 2 \times 10^4$ dm^3 mol^{-1} cm^{-1}), increasing in wavelength with the length of conjugated chain, $R(C{\equiv}C\text{–}CH{=}CH)_nC{\equiv}CR'$, $n = 1$, 2 or 3 (see Table 1). Similar trends have been reported for the compounds with $R = R' = {}^tBu$ [18]. Replacing $R/R' = SiMe_3$ or ^tBu by $R/R' = Ph$ causes bathochromic shifts of the absorption bands which are greater for the shorter chain compounds, indicating that the terminal substituents have less influence on the energy levels of the longer conjugated systems. Coordination of $Co_2(CO)_6$ or $Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ units to the alkyne bonds of the conjugated chains produces low energy bands in the visible region, 550–580 nm, accompanied by other new bands in the visible or near UV (see Table 1). The reported UV-visible spectra of simple alkyne complexes $[Co_2(C_2R_2)(CO)_6]$ include a band at λ_{max} 345–366 nm (ϵ *ca.* 10^4), with more intense bands below 300 nm; weaker bands have been reported in the visible region for some derivatives, with λ_{max} values in the ranges 410–430 and 515–560 nm (*e.g.* 540 nm (ϵ 280) for R = H; 555 nm (ϵ 670) for R = Ph) [19]. $[Mo_2(C_2H_2)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ is reported to show bands with maxima at 361 nm (ϵ 7400) and 533 nm (ϵ 850) assigned, respectively, to $\sigma \rightarrow \sigma^*$ and $\pi\text{-}d \rightarrow \sigma^*$ transitions [20], but these energy levels must be somewhat modified by interaction with the conjugated chain of the ynene ligands in the compounds of this study. The wavelength of the lowest energy transition of complexed E-$Me_3SiC{\equiv}C\text{–}CH{=}CH\text{–}C{\equiv}CSiMe_3$ increases as coordination is extended from one to both alkyne functions, *i.e.* from 550 to 575 nm for cobalt and from 560 to 570 nm for molybdenum.

Table 1

UV-visible data for selected free ynenes and coordinated ynenes [a]

		λ_{max} nm ($\epsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1})			
E-$Me_3SiC{\equiv}CCH{=}CHC{\equiv}CSiMe_3$	**(3a)**	261sh (1.7)	269 (2.6)	273 (2.3)	286 (2.8)
Mono-$Co_2(CO)_6$	**(7a)**	320sh (2.4)	440sh (0.13)	550 (0.09)	
Bis-$Co_2(CO)_6$	**(6a)**	330sh (2.0)	340sh (2.0)	575 (0.25)	
Mono-$Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$	**(7b)** [b]	320sh (1.9)	350sh (1.2)	425sh (0.44)	560 (0.14)
Bis-$Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2$	**(6e)** [b]	315sh (1.6)	355sh (1.5)	430sh (0.48)	570 (0.22)
E-$PhC{\equiv}CCH{=}CHC{\equiv}CSiMe_3$	**(3c)**	283sh (1.5)	292 (1.7)	302 (2.3)	
		308sh (2.1)	323 (2.5)		
Bis-$Co_2(CO)_6$	**(6c)**	310sh (2.1)	340sh (1.8)	575 (0.2)	
E-$HC{\equiv}CCH{=}CHC{\equiv}CH$	**(3b)** [c]	254 (2.5)	264 (2.3)		
Bis-$Co_2(CO)_6$	**(6b)**	330sh (2.0)	565 (0.23)		
E,E-$Ph(C{\equiv}CCH{=}CH)_2C{\equiv}CPh$	**(4)** [d]	355 (4.6)	380sh (3.5)		
Tris-$Co_2(CO)_6$	**(9)** [b]	325sh (2.2)	350sh (1.8)	575 (0.19)	
E,E,E-$Ph(C{\equiv}CCH{=}CH)_3C{\equiv}CPh$	**(5)** [d]	378 (6.33)	388 (5.7)		
Tetrakis-$Co_2(CO)_6$	**(10)** [b]	320sh (4.4)	350sh (5.1)	580 (0.6)	

[a] In n-hexane, unless otherwise stated. [b] In CH_2Cl_2. [c] From ref. 6 (in THF). [d] In $CHCl_3$.

Maximum coordination of $Co_2(CO)_6$ to two, three or four adjacent alkyne bonds in ligands all-*trans* $R(C{\equiv}C\text{–}CH{=}CH)_nC{\equiv}CR'$ with $n = 1$, 2 or 3, respectively, causes little difference (*ca.* 5 nm) in λ_{max} of the observed low energy electronic transition, although there is an increase in intensity related to the increase in the number of complexed alkyne bonds. Thus, although electronic transitions associated with the dicobalt tetrahedrane chromophore are influenced by the conjugated ynene chain of the ligand, it appears that the maximum shift in the visible absorption bands occurs when two adjacent alkyne bonds are coordinated to dicobalt entities.

Experimental

Organometallic reactions were carried out under dry nitrogen by standard Schlenk techniques. Solvents used were dried under reflux and freshly distilled under dry nitrogen before use. Drying agents were: Na/benzophenone (for 60–80°C petroleum ether, diethyl ether, tetrahydrofuran (THF), and toluene); and P_2O_5 (for dichloromethane). Infrared spectra were recorded on Perkin–Elmer 580 and 1600 instruments and calibrated against polystyrene. ^1H NMR spectra were recorded on Jeol PX 60 (60 MHz), Bruker WP80 (80 MHz), or Bruker WP200 (200.13 MHz) spectrometers. ^{13}C NMR spectra were recorded on a Bruker WP200 (50.32 MHz) spectrometer. Chemical shifts are reported with respect to tetramethylsilane as reference (positive shifts to high frequency/low field). 400 MHz NMR spectra were recorded using the SERC service at Warwick University. UV-visible spectra were recorded on a Shimadzu UV-240 spectrophotometer. Elemental analyses were performed at UMIST, Manchester, UK.

*Z- and E-1,6-Bis(substituted)hexa-1,5-diyn-3-enes, **2a,b** [7] and **3a** [6]*

These compounds were prepared by published methods. Spectral data for compound **3a**: ^1H NMR (200 MHz, $CDCl_3$): δ 5.99 (s, 2H, =CH–); 0.17 (s, 18H,

$Si(CH_3)_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 121.7 (=CH–); 102.9 and 100.2 (C≡C); −0.2 ($Si(CH_3)_3$).

E-*Hexa-1,5-diyn-3-ene (3b)*

This was prepared by desilylation (LiOH, aq. THF) [9] of **3a** and was stored in n-pentane at −25°C. It was sufficiently stable in DMSO-d_6 at room temperature to record a ^1H NMR spectrum: δ 4.35 (s, 2H, ≡CH); 6.15 (s, 2H, =CH–).

Preparation of E-*1-phenyl-6-trimethylsilylhexa-1,5-diyn-3-ene (3c)*

A solution of trimethylsilylacetylene [21] (0.75 g, 7.6 mmol) in dry THF (15 ml) was cooled to −78°C. To this was slowly added 4.6 ml of 1.6 *M* ethyl magnesium bromide in diethyl ether. The thick white suspension was then allowed to warm to room temperature over a period of 2 h, and then the mixture was heated under reflux for 1 h. It was then cooled to −78°C and *E*-1-chloro-4-phenyl-1-buten-3-yne [8] (1.0 g, 6.1 mmol) and [$NiCl_2$(dppp)] (0.056 g, 0.1 mmol) were added in sequence, with stirring. The mixture was allowed to warm slowly to room temperature and stirring was continued for 12 h. The product was quenched by pouring into saturated ammonium chloride solution (150 ml). The organic phase was separated, washed with water (20 ml), then brine (20 ml), and was dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (60–80°C petroleum ether as eluant) to yield *E*-1-phenyl-6-trimethylsilylhexa-1,5-diyn-3-ene (**3c**) (1.1 g, 65%) as a pale yellow oil. Anal. Found: C, 80.5; H, 7.3. $C_{15}H_{16}Si$ calc.: C, 80.3, H, 7.19%. ^1H NMR (200 MHz, $CDCl_3$): δ 7.44 (m, 2H, Ph); 7.32 (m, 3H, Ph); 6.24 (d, 1H, $J = 16.1$ Hz, =CH–); 6.07 (d, 1H, $J = 16.1$ Hz, =CH–); 0.21 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 131.6, 128.6 and 128.3 (*o*-, *m*-, *p*- C, Ph); 122.8 (*ipso*-C, Ph); 121.9 and 120.5 (=CH–); 103.2, 100.5, 95.0 and 87.7 (≡C); −0.2 ($Si(CH_3)_3$). IR (neat): 3080w, 3060w, 3030m, 2960s, 2920s, 2900m, 2850m, 2060m, 2020s, 1750m, 1600m, 1485s, 1440m, 1290m, 1250s, 1075s, 930s, 850s, 755s, 685s and 650s cm^{-1}. MS (EI, 70 eV): *m/z* 224(7), 209(9).

Desilylation of E-*1-phenyl-6-trimethylsilylhexa-1,5-diyn-3-ene: preparation of* E-*1-phenylhexa-1,5-diyne-3-ene (3d)*

A mixture of lithium hydroxide (0.25 g, 10.4 mmol), *E*-1-phenyl-6-trimethylsilylhexa-1,5-diyne-3-ene (**3c**) (0.40 g, 1.78 mmol), THF and water (0.25 ml) was stirred at room temperature for 2 h. The organic and aqueous layers were separated and the aqueous portion was washed with pentane (3 × 5 ml). The combined organic extract was dried over anhydrous potassium carbonate, filtered through Celite, and then washed with further pentane (10 ml). The solvent was evaporated under reduced pressure to give the title compound **3d** as a clear oil. It was unstable at room temperature and was stored at −20°C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.44 (m, 2H, Ar–H); 7.33 (m, 3H, Ar–H); 6.31 (A component of ABX system, 1H, $J_{AB} = 16.1$ Hz, $J_{AX} = 0.55$ Hz, =CH–); 6.04 (B component of ABX system, 1H, $J_{AB} = 16.1$ Hz, $J_{BX} = 2.35$ Hz, =CH–); 3.2 (X component of ABX system, *dd*, 1H, ≡CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 131.6, 128.7 and 128.35 (*o*-, *m*-, *p*- C, Ph); 122.65 (*ipso*-C, Ph); 122.9 and 119.5 (=CH–); 95.0 and 87.3 (C≡C–Ph); 82.35 and 81.9 (C≡C–H).

Preparation of E,E-*1,10-diphenyldeca-1,5,9-triyn-3,7-diene (4)*

A solution of *E*-1-phenylhexa-1,5-diyn-3-ene (**3d**) (1.49 g, 9.8 mmol) in dry THF (25 ml) was cooled to −78°C (dry ice/acetone), and to this was slowly added ethylmagnesium bromide (1.33 g, 0.01 mol) in diethyl ether (20 ml). The resulting white/yellow suspension was allowed to warm slowly to room temperature over 2 h and then heated at 60°C for 10 min. The solution was then cooled to −78°C and *E*-1-chloro-4-phenyl-1-buten-3-yne [8] (1.58 g, 9.8 mmol) and [$NiCl_2$ (dppp)] (0.075 g, 0.014 mmol) were added in sequence. The mixture was stirred at 5°C for 30 h and then poured into saturated ammonium chloride solution (100 ml). The organic layer was separated and washed with water (2 × 20 ml), then brine (2 × 20 ml), and was finally dried over anhydrous sodium carbonate. The resulting solution was evaporated to low volume and chromatographed on neutral alumina (pentane eluant) to yield the title compound **4** as a pale yellow solid (365 mg, 13%), m.p. 90–92°C. Anal. Found: C, 94.7; H, 5.1. $C_{22}H_{14}$ calc.: C, 94.9; H, 5.07%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.50 (m, 4H, Ph); 7.38 (m, 6H, Ph); 6.30 (s, 4H, C=CH). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 132.0, 129.5 and 129.2 (*o*-, *m*-, *p*- C, Ph); 123.2 (*ipso*-C, Ph); 122.55 and 120.7 (=CH–); 96.1, 94.0 and 88.5 (≡C–). IR (KBr): 3040w, 3030w, 2190w, 1755w, 1595w, 1480m, 930s, 750s and 690s cm^{-1}. MS (LIMA): *m/z* 278 ($M^{\cdot+}$).

Preparation of E,E,E-*1,14-diphenyltetradeca-1,5,9,13-tetrayn-3,7,11-triene (5)*

A solution of *E*-1-phenylhexa-1,5-diyn-3-ene (**3d**) (0.80 g, 5.3 mmol) in dry THF (25 ml) was cooled to −78°C (dry ice/acetone), and to this was slowly added ethylmagnesium bromide (0.7 g, 5.3 mmol) in diethyl ether (20 ml) with stirring; the resulting white suspension was allowed to warm to room temperature over 2 h and then heated under reflux for 30 min, whereupon the colour of the solution changed from pale yellow to brown. The solution was then cooled to −78°C and *E*-1,2-dichloroethylene (0.204 g, 2.1 mmol) and [$NiCl_2$(dppp)] (0.0384 g, 0.0071 mmol) were added in sequence. The mixture was then slowly warmed to room temperature and stirring continued for 12 h. The product was poured into saturated ammonium chloride solution (150 ml). The organic phase was separated, washed with water (2 × 20 ml) and then brine (2 × 20 ml), and finally dried over Na_2SO_4. The mixture was then purified by column chromatography (silica gel, n-hexane eluant). The title compound **5**, [0.10 g (10%)], m.p. 162°C (dec), was a pale yellow solid which decolourized on exposure to light. It proved impossible to obtain satisfactory data from elemental analysis. Anal. Found: C, 91.8; H, 4.75. $C_{26}H_{16}$ calc.: C, 95.1; H, 4.9%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.45 (m, 4H, Ph); 7.35 (m, 6H, Ph); 6.26 (s, 4H, =CH–); 6.20 (s, 2H, =CH–). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 132.0, 129.3 and 128.9 (*o*-, *m*-, *p*- C, Ph); 123.15 (*ipso*-C, Ph); 122.1, 121.4 and 120.6 (=CH–), 96.2, 94.8, 93.9 and 85.3 (≡C–). IR (KBr): 3030w, 2200w, 2175w, 1755m, 1620w, 1600w, 1580w, 1485m, 1440m, 935s, 760s and 690s cm^{-1}. MS (LIMA): *m/z* 328 ($M^{\cdot+}$).

Preparation of E-*1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene bis(hexacarbonyldicobalt) (6a)*

Octacarbonyldicobalt (0.44 g, 1.29 mmol) and *E*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene (**3a**) (0.14 g, 0.64 mmol) in petroleum ether (b.p. 60–80°C) (30 ml) was stirred for 24 h at room temperature, the colour changing from yellow/brown to black. The solution was evaporated to low volume and purified by column chromatography on silica gel (petroleum ether, b.p. 60–80°C eluant) to give a single black band which yielded the title compound **6a** (0.45 g, 89%) as a black crystalline solid. Anal. Found: C, 36.7; H, 2.2. $C_{24}H_{20}O_{12}Si_2Co_4$ calc.: C, 36.38; H, 2.54%. ^{1}H NMR (200 MHz, C_6D_6): δ 7.33 (s, 2H, C=CH); 0.23 (s, 18H, $Si(CH_3)_3$). ^{13}C (50 MHz, C_6D_6): δ 199.9 (CO); 132.1 (C-3 and C-4); 101.9 (C-2 and C-5); 81.05 (C-1 and C-6); 0.3 ($Si(CH_3)_3$). IR (n-hexane): ν(CO) 2090m, 2080s, 2065s, 2015s, 2010s and 1975w cm^{-1}. MS (EI, 70 eV): m/z 792 (1%, $M^{\cdot+}$), 764(3), 736 (3), 708 (1), 680 (5), 652 (5), 624 (8), 596 (23), 568 (11), 540 (9), 512 (6), 484 (6), 456 (5), 220 (4), 147 (39), 73 (69), 59 (82).

Preparation of E*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene hexacarbonyldicobalt (7a)*

Octacarbonyldicobalt (0.30 g, 0.87 mmol) and *E*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene (**3a**) (0.19 g, 0.86 mmol) in n-hexane (25 ml) was stirred at room temperature for 24 h. The product was chromatographed (silica gel, n-hexane eluant) to yield three fractions, the first of which gave the black crystalline bis-hexacarbonyldicobalt complex **6a** (40 mg, 12%). The middle band was a mixture of red and black components, and the final fraction was the mono-hexacarbonyldicobalt complex **7a** as a red oil (80 mg, 18%). Anal. Found: C, 41.4; H, 3.3. $C_{18}H_{20}O_6Si_2Co_2$ calc.: C, 42.69; H, 3.95%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.17 (d, 1H, J = 15.4 Hz, H_A); 6.02 (d, 1H, J = 15.3 Hz, H_B); 0.32 (s, 9H, $Si(CH_3)_3$); 0.22 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 200.2 (CO); 140.6 (C-3); 114.0 (C-4); 104.2, 101.0 and 99.5 (C-2, C-5 and C-6)); 81.9 (C-1); 0.7 and −0.1 ($Si(CH_3)_3$). IR (n-hexane): ν(CO) 2085m, 2050s, 2025s, 2020s, 2000m and 1980vw cm^{-1}. MS (EI, 70 eV): m/z 506 ($M^{\cdot+}$) 478 (6), 450 (10), 422 (12), 394 (33), 366 (62), 338 (12), 279 (10), 220 (8), 205 (30), 73 (20).

Preparation of E*-hexa-1,5-diyn-3-ene bis(hexacarbonyldicobalt)* ***(6b)***

To a degassed solution of *E*-hexa-1,5-diyn-3-ene (**3b**) (0.17 g, 2.2 mmol) in n-pentane (20 ml) was added octacarbonyldicobalt (1.55 g, 4.53 mmol), and the mixture was stirred for 2 days. The product was evaporated to low volume and purified by column chromatography (silica gel, n-hexane eluant) to yield the title compound **6b** as a purple/black solid (0.56 g, 38%). Anal. Found: C, 33.1; H, 0.6%. $C_{18}H_4O_{12}Co_4$ calc.: C, 33.3; H, 0.62%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.12 (s, 2H, =CH–); 6.36 (s, 2H, ≡CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 199.7 (CO); 132.7 (C-3 and C-4); 87.45 (C-2 and C-5); 74.6 (C-1 and C-6). IR (n-hexane): ν(CO) 2100m, 2085s, 2060s, 2030s and 1985w cm^{-1}. MS (EI, 70 eV): m/z 648 (0.07, $M^{\cdot+}$), 620 (0.09), 592 (0.13), 564 (0.10), 536 (0.08), 508 (0.12), 480 (0.16), 452 (0.34), 424 (0.39), 395.9 (0.16), 368 (0.19), 340 (0.17) and 312 (0.25).

Preparation of Z*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene hexacarbonyldicobalt (8)*

A solution of octacarbonyldicobalt (0.32 g, 0.94 mmol) and *Z*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene (**2a**) (0.107 g, 0.49 mmol) in n-hexane (30 ml) was stirred at room temperature for 24 h. The product was purified by column chromatography (silica gel, n-hexane eluant) to yield the title compound **8** as a red oil (0.183 g, 74%). Anal. Found: C, 42.4; H, 3.9. $C_{18}H_{20}O_6Si_2Co_2$ calc.: C, 42.69; H, 3.95%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 6.82 (d, 1H, J = 11.2 Hz, H_A); 5.95 (d, 1H, J = 11.2 Hz, H_B); 0.36 (s, 9H, $Si(CH_3)_3$); 0.21 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (50 MHz,

CD_2Cl_2): δ 200.05 (CO); 137.2 (C-3); 111.8 (C-4); 107.5, 103.4, 96.1 (C-2, C-5 and C-6); 82.2 (C-1), 1.0; −0.1 ($Si(CH_3)_3$). IR (n-hexane): ν(CO) 2085m, 2030s, 2025s, 2020s, 2000sh and 1985w. MS (EI, 70 eV): *m/z* 506 ($M^{\cdot+}$), 478 (8), 450 (28), 422 (24), 394 (68), 366 (100), 338 (26), 279 (61), 220 (3), 205 (12), 73 (38).

Preparation of E-*1-phenyl-6-trimethylsilylhexa-1,5-diyn-3-ene bis(hexacarbonyldicobalt)* (**6c**)

Octacarbonyldicobalt (1.09 g, 3.18 mmol) and *E*-1-phenyl-6-trimethylsilylhexa-1,5-diyn-3-ene (**3c**) (0.356 g, 1.59 mmol) in n-hexane (25 ml) was stirred for 24 h, the colour of the solution changing from yellow/brown to dark red/black. Most of the solvent was then removed under reduced pressure and the residue was purified by column chromatography (silica gel, n-hexane eluant) to yield the title compound **6c** as a black/red solid (0.98 g, 77%). Anal. Found: C, 40.4; H, 1.8. $C_{27}H_{16}O_{12}Co_4Si$ calc.: C, 40.7; H, 2.03%. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.57 (m, 2H, Ph); 7.37 (m, 3H, Ph); 7.32 (d, 1H, $J = 14.4$ Hz, H_A or H_B); 7.23 (d, 1H, $J = 14.4$ Hz, H_B or H_A); 0.36 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 199.5 (CO); 138.6 (*ipso*-C, Ph); 133.3 and 132.5 (C-3 and C-4); 129.7, 129.4 and 128.55 (*o*-, *m*-, *p*- C, Ph); 102.4 (C-5); 93.25 and 89.6 (C-1 and C-2); 81.65 (C-6); 0.7 ($Si(CH_3)_3$). IR (n-hexane): ν(CO) 2100m, 2085m, 2060s, 2057sh, 2030s and 1980vw cm^{-1}. MS (EI, 70 eV): *m/z* 796 (0.2, $M^{\cdot+}$), 768 (0.3), 740 (0.2), 712 (0.3), 684 (0.6), 656 (0.8), 628 (2.6), 73 (29), 59 (41).

Preparation of E-*1-phenylhexa-1,5-diyn-3-ene bis(hexacarbonyl dicobalt)* (**6d**)

E-1-Phenylhexa-1,5-diyn-3-ene (**3d**) (175 mg, 1.15 mmol) (30 ml) and octacarbonyldicobalt (0.80 g, 2.3 mmol) in n-pentane (30 ml) was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the product was purified by column chromatography (silica gel, n-hexane eluant) to give the title compound **6d** as a red/black oil (0.49 g, 60%). This compound gradually decomposed on standing, even at −20°C, and it proved impossible to obtain satisfactory data from elemental analysis. Anal. Found: C, 37.8; H, 1.4. $C_{24}H_8O_{12}Co_4$ calc.: C, 39.8; H, 1.11%. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.6 (m, 2H, Ph); 7.35 (m, 4H, Ph, C=CH); 7.2 (d, 1H, C=CH); 6.37 (s, 1H, C≡CH). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 199.5 (CO); 138.65 (*ipso*-C, Ph); 133.5 and 132.8 (C-3 and C-4); 129.7, 129.4 and 128.5 (*o*-, *m*-, *p*- C, Ph); 93.3 and 89.7 (C-1 and C-2); 87.7 (C-5); 74.8 (C-6). IR (n-hexane): ν(CO) 2095w, 2085m, 2060s, 2030s and 2010sh cm^{-1}. MS (FAB NOBA matrix): *m/z* 695 ($M^{\cdot+}$ − H, CO), 667, 639, 611, 583, 555 (base), 527, 449, 471, 445, 416, 388.

Preparation of E,E-*1,10-diphenyldeca-1,5,9-triyn-3,7-diene tris(hexacarbonyldicobalt)* (**9**)

A solution of octacarbonyldicobalt (0.295 g, 0.86 mmol) and *E*,*E*-1,10-diphenyldeca-1,5,9-triyn-3,7-diene (**4**) (0.080 g, 0.29 mmol) in n-hexane (50 ml) was stirred for 24 h at 5°C. The solution was evaporated to low volume under reduced pressure and the product was purified by column chromatography (silica gel, n-hexane eluant) to give a single green band which yielded the title compound **9** as a black/green solid (0.283 g, 85%). Anal. Found: C, 42.5; H, 1.3; Co, 31.1. $C_{40}H_{14}O_{18}Co_6$ calc.: C, 42.3; H, 1.24; Co, 31.1%. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.6 (m, 4H, Ph); 7.35 (m, 10H, Ph and =CH–). ^{13}C NMR (50 MHz, CD_2Cl_2): δ

199.45 (CO); 138.6 (*ipso*-C, Ph); 133.2 (=CH–); 129.67, 129.5 and 128.6 (*o*-, *m*-, *p*-C, Ph); 93.4, 90.4 and 89.6 (≡C–). IR (n-hexane): ν(CO) 2090w, 2085m, 2080m, 2055s, 2010s and 1985vw cm^{-1}. MS (FAB): *m/z* 1052 ($M^{\cdot+}-3CO$), 940 ($M^{\cdot+}-6CO$).

Preparation of E,E,E-*1,14-diphenyltetradeca-1,5,9,13-tetrayn-3,7,11-triene tetrakis (hexacarbonyldicobalt) (10)*

A solution of octacarbonyldicobalt (0.248 g, 0.73 mmol) and *E*,*E*,*E*-1,14-diphenyltetradeca-1,5,9,13-tetrayn-3,7,11-triene (**5**) (0.056 g, 0.17 mmol) in toluene (60 ml) was stirred for 24 h, the colour of the solution changing from yellow/brown to green/black. The toluene was evaporated under reduced pressure and the residual solid was washed with hexane and dried under vacuum, to yield the title compound **10** as a black/green solid (0.228 g, 90%), m.p. 270°C (dec.) Anal. Found: C, 40.5; H, 1.4; Co, 31.6. $C_{50}H_{16}O_{24}Co_8$ calc.: C, 40.8; H, 1.1; Co, 32.0%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.6 (m, ≡CH and Ph). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 199.1 (CO); 132.9 (=CH–); 132.5 (*ipso*-C, Ph); 129.4, 129.1 and 128.3 (*o*-, *m*-, *p*- C, Ph); *ca.* 90 (br, C≡C) IR (CH_2Cl_2): ν(CO) 2090m, 2065s and 2025s cm^{-1}. MS (FAB, NOBA matrix): *m/z* 1387 ($M^{\cdot+}-CO$), 1303 ($M^{\cdot+}-6CO$).

Preparation of E-*1,6-bis(trimethylsilyl)hexa-1,5-diyne-3-ene bis(di-η^5-cyclopentadienyltetracarbonyldimolybdenum) (6e)*

E-1,6-Bis(trimethylsilyl)hexa-1,5-diyne-3-ene (**3a**) (0.15 g, 0.68 mmol) was added to a solution of $[CpMo(CO)_2]_2$ [12a] (0.56 g, 1.3 mmol) in toluene (25 ml) and the mixture was stirred for 12 h. The toluene was then evaporated under reduced pressure, and the residue washed with diethyl ether (4 × 20 ml). The residual material was dissolved in dichloromethane (60 ml) and the mixture was filtered. Evaporation of the dichloromethane under reduced pressure yielded the title compound **6e**, a black solid (0.57 g, 78%). Anal. Found: C, 43.1; H, 3.7; Mo, 34.0. $C_{40}H_{40}O_8Si_2Mo_4$ calc.: C, 44.1; H, 3.68; Mo, 35.3%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.82 (s, 2H, =CH–); 5.25 (s, 20H, C_5H_5); 0.20 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 230.6 and 229.6 (CO); 134.75 (C-3, C-4); 90.65 (C_5H_5): 1.8 ($Si(CH_3)_3$) (resonances for C≡C not observed). IR (CH_2Cl_2): ν(CO) 1980m, 1959sh, 1925s and 1835m cm^{-1}. MS (FAB, NOBA matrix): *m/z* 1089 $(M+H)^{\cdot+}$, 892 ($M^{\cdot+}-7CO$).

Preparation of E-*1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene(di-η^5-cyclopentadienyltetracarbonyldimolybdenum) (7b)*

A solution of *E*-1,6-bis(trimethylsilyl)hexa-1,5-diyn-3-ene (**3a**) (0.125 g, 0.57 mmol) was added to a solution of $[CpMo(CO)_2]_2$ [12a] (0.296 g, 0.68 mmol) in toluene (25 ml) and the mixture was stirred at room temperature for 12 h. The solution was evaporated under reduced pressure to low volume, and chromatographed (silica gel, n-hexane eluant). A red/purple band was collected and the product recrystallized from n-hexane to yield the title compound **7b** as a purple crystalline solid (70 mg, 19%). Anal. Found: C, 47.6; H, 4.8. $C_{26}H_{30}O_4Si_2Mo_2$ calc.: C, 47.7; H, 4.62%. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.30 (d, 1H, $J=15.6$ Hz, H_A); 5.48 (d, 1H, $J=15.6$ Hz, H_B); 5.28 (s, 10H, C_5H_5); 0.20 (s, 9H, $Si(CH_3)_3$); 0.07 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 212.0 and 210.8 (CO); 148.7 (C-3); 107.6 (C-4) 7; 108.2, 104.5 and 96.4 (C-2, C-5 and C-6); 91.7 (C-1); 91.6

(C_5H_5); 2.0 and 0.2 ($Si(CH_3)_3$). IR (n-hexane): ν(CO) 1995m, 1940s, 1930s and 1855m cm^{-1}. MS (EI, 70 eV): *m/z* 658 (2%, $M^{\cdot+}$), 630 (0.44), 602 (2), 574 (5), 546 (13), 270 (3), 205 (10), 73 (24).

On further elution with dichloromethane, a black band was eluted which yielded a black solid (30 mg 5%); this was identical to compound **6e**, described above.

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