ORGANOMETALLICS-

Synthesis and Properties of New Dimeric η^2 -Diyne Complexes of Cobalt Linked through an Azobenzene Ligand

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Supporting Information

ABSTRACT: The reaction between 4,4'-diiodoazobenzene (**0**) with excess trimethylsilylacetylene or dec-1-yne in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI, Sonogashira coupling conditions, gave rise to the formation of 4,4'-bis(trimethylsilylethynyl)azobenzene (**1**) and 4,4'-bis(dec-1-ynyl)azobenzene (**2**), in good yield, in addition to icosa-9,11-diyne (**3**) as byproduct in the last case. The analogous reactions from **0** and the alkynyl-cobalt complexes $Co_2(CO)_4(\mu$ -L-L) $(\mu_2 \cdot \eta^2$ -SiMe₃C₂)](C=CH) (L-L = dppm, dmpm) afforded **12–14**. Complexes **4**–7 and **15** have been obtained by direct reaction between $Co_2(CO)_8$ and the organic ligands **1**–3. In order to increase the stabilization of Co–Co bonds, diphenylphosphinomethane-substituted alkyne-carbonyl complexes **8–11** were prepared by substitution reaction of carbonyl ligands in the presence of Me₃NO at the $Co_2(CO)_6$ units from **4**–7. All products were characterized by analytical and spectroscopic data (IR, ¹H, ¹³C, and ³¹P NMR, and MS). Crystals of **9** suitable for single-crystal X-ray diffraction were grown, and the molecular structure of this compound is discussed. In this paper we report a comparative electrochemical study of these complexes by means of cyclic and square-wave voltammetry techniques, the *trans–cis* photoisomerization study of azobenzene compounds, and the thermotropic liquid-crystalline behavior.



INTRODUCTION

Azobenzene and its derivatives constitute a family of dye molecules known since the middle of the last century.¹ These chromophores are very versatile molecules that have received much attention in both fundamental and applied research areas.² Basically, they are characterized by intense color, high thermal stability (up to 350 °C), and a trans to cis reversible isomerization of the N=N double bond upon UV light irradiation, whereas the reverse isomerization can take place by visible light irradiation or by heating, the trans-form being generally more stable than the cis-form.³ Photoinduced isomerization involves dramatic structural rearrangements: the distance between the para carbon atoms in the molecule decreases from about 9.0 Å in the trans-form to 5.5 Å in the cisform. Furthermore, the change in the configuration leads to a significant increase in the dipole moment. The trans-form has no dipole moment, while the dipole moment of the nonplanar cis compound is 3.0 D.⁴

Azobenzene and nearly all its monosubstituted derivatives show a strong band in the UV region attributed to the $\pi-\pi^*$ transition at ca. 290 nm in the *cis*-form (depending on the solvent) and at ca. 320 nm in the *trans*-form and a much weaker band in the visible region (around 450 nm), due to the $n-\pi^*$ transition.⁵ On conversion to the *cis*-isomer, the $\pi-\pi^*$ band shifts to shorter wavelengths, and the intensity of the $n-\pi^*$ absorption increases. Usually, four mechanisms for the *trans*-*cis* reaction are considered: rotation, inversion, concerted inversion, and inversion-assisted rotation. The actual mechanism depends on the exact surroundings of the azo group.^{3,6}

Since the two isomers exhibit well-separated absorption bands in the UV–visible region and different physical properties, such as dielectric constant and refractive index, and azo polymers are also found to have liquid-crystalline (LC) properties due to the rod-like nature of the azobenzene moiety, azobenzene and its derivatives are good candidates for many applications such as light-triggered switches,⁷ constituents of erasable holographic data, image storage devices and materials with photomodulable properties,^{3–8} and a possible basis for a light-powered molecular machine.⁹

The combination of these remarkable photoswitching properties of azobenzene with the electrochemical, magnetic, catalytic, or biological properties of the metal complexes could give rise to multifunctional molecules.¹⁰ In many of these metal species, the ligand is chelated to the metal through one of the nitrogen atoms and either a second nitrogen donor substituent or a carbon atom, so that the photoisomerization of the azo group is not possible.¹¹ Only a few organometallic compounds are known in which the azo group is free to undergo isomerization.¹²

The chemistry of cobalt with any azo ligand is limited up to the present to a few coordination cobalt complexes;¹³ for this reason we wished to explore the chemistry of organometallic

Received: April 8, 2015

Table 1. ¹ H NMR Data in CDCl ₃ Solution of 4, 5, 8,	and 9 (Obtained from 1), 6, 7, 10,	, and 11 (Obtained from 2), and 12–14
(in Comparison with 1 and 4,4'-Diiodoazobenzene	$(0))^{a}$	

	H _{2,2}	H _{3,3}	H _{6,6}	H _{7,7}		H _{2,2}	H _{3,3}	H _{6,6}	H _{7,7}		H _{2,2}	H _{3,3}	H _{6,6}	H _{7,7}
1	7.86	7.60			2	7.83	7.51			1	7.86	7.60		
4	7.86	7.60	7.89	7.64	6	7.86	7.53	7.89	7.62	0	7.70	7.84		
5			7.90	7.65	7			7.91	7.63	12	7.68	7.88	7.90	7.46
8	7.89	7.63	7.73	7.25	10	7.86	7.53	7.75	7.33	13			7.99	7.54
9			7.69	7.21	11			7.76	7.32	14	7.69	7.91	7.91	7.54
^a All th	'All the signals appear as doublets with $J_{\rm HH} \approx 8.5$ Hz.													

Table 2. ¹³C NMR Data in $CDCl_3$ Solution of 4, 5, 8, and 9 (Obtained from 1), 6, 7, 10, and 11 (Obtained from 2), and 12 and 13 (Obtained from 0)

	C_1	C _{2,2'}	C _{3,3'}	C_4	C ₅	C _{6,6'}	C _{7,7′}	C ₈	$C_9 \equiv C_{10}$	$C_{11} - C_{12}$
1	152.4	122.6	132.6	124.9					105.8; 94.2	
4	151.8	122.8	132.9	125.9	152.1	123.6	130.6	142.1	104.7; 97.3	103.7; 80.3
5					152.0	123.6	130.7	142.0		103.8; 80.3
8	152.3	122.7	132.9	125.4	150.6	123.1	130.4	148.9	104.8; 97.0	104.7; 90.1
9					150.9	122.9	130.5	147.9		104.8; 89.8
	C_1	C _{2,2'}	C _{3,3'}	C_4	C ₅	C _{6,6'}	C _{7,7′}	C ₈	$C_9 \equiv C_{10}$	$C_{11} - C_{12}$
2	151.3	122.8	132.3	127.0					93.5; 80.5	
6	151.5	122.8	132.4	127.1	151.7	123.5	129.9	142.0	93.6; 80.5	100.7; 89.7
7					151.8	123.4	129.9	142.1		100.8; 89.7
10	151.7	122.6	132.3	126.5	150.4	123.0	129.5	148.5	93.2; 80.6	105.5; 92.5
11					150.8	122.9	129.8	147.7		105.9; 92.7
	C_1	$C_{2,2'}$	C _{3,3'}	C_4	C ₅	C _{6,6'}	C _{7,7'}	C ₈	$C_9 \equiv C_{10}$	$C_{11} - C_{12}$
0	151.7	124.6	138.2	97.4						
12	152.1	124.5	138.5	97.8	150.9	123.2	131.8	96.9	82.4; 94.7	90.5; 76.7
13					151.3	123.1	131.8	96.8	82.9; 94.8	90.7; 76.6

Scheme 1





CH3-(CH2)7

 $(CO)_{2}$

Me₂S SiMe₃ 12 Co(CO)₂ $(CO)_{2}(CO)$ 20(CO)2 (CO)₂ PR₂ CH2-PR ĆΗ₂ R = Ph(dppm) (13)

redox cobalt centers linked through the azobenzene fragment in order to evaluate the effect of the organometallic group in the azobenzene properties as trans-cis isomerization or redox behavior. Thus, in this paper we report the synthesis, characterization, redox properties, a detailed trans-cis-trans isomerization study that aims at clarifying the role played by trans substituents, and the mesomorphic behavior of several para-alkynyl azobenzene derivatives (R-Azo-R) and their organometallic cobalt complexes linked to the azobenzene unit by a π -conjugated carbon bridge.

RESULTS AND DISCUSSION

R₂

Synthesis and Characterization. 1 and 2 have been synthesized from coupling reactions of 4,4'-diiodoazobenzene (0) with excess trimethylsilylacetylene (TMSA) and 1-decyne, respectively, under Sonogashira coupling conditions. From 0 and 1-decyne we have obtained the desired dialkynyl organic ligand 2, in addition to icosa-9,11-diyne $(3)^{14}$ as a secondary product, caused by a side reaction of the terminal acetylene with itself. Moreover the nonanoic acid has also been obtained as byproduct in this reaction, probably because terminal alkynes can undergo oxidative $C \equiv C$ cleavage to afford the corresponding carboxylic acid and CO_2 . 1 and 2, which have been completely characterized by analytical and spectroscopic data (details of which are given in the Experimental Section), show in the ¹H NMR spectra two doublet signals due to the azobenzene ring protons, with coupling constants that are consistent with their chemical formulations, and in the ¹³C NMR spectra six singlet signals belonging to the azobenzene rings $(C_1, C_{2,2'}, C_{3,3'}, and C_4)$ and the alkynyl units $(C_9 and C_9)$ C_{10}), in addition to the corresponding signals due to the carbon chain in 2 (Tables 1 and 2). The assignments were made on the basis of the δ values and two-dimensional NMR experiments (HMBC and HMQC). The FT-IR spectrum of 1 in CH₂Cl₂ displays a weak absorption band, typically C≡C stretches of the alkynyl unit, in the characteristic range of monoynyl complexes (one $\nu_{C \equiv C}$ stretch at ca. 2090–2160 cm⁻¹) that could not be observed in 2. Both organic ligands gave

satisfactory mass spectrometric data. Co₂(CO)₆-substituted alkyne complexes 4-7 were synthesized by direct reaction between $Co_2(CO)_8$ and the organic ligand 1 or 2 after separation and purification by TLC silica plates using hexane/ CH₂Cl₂ (2:1 or 3:1) as eluent (see Scheme 1). In order to enhance the stability of the dicobalt units in 4-7 by a bridging effect between the two metal atoms, we have also prepared complexes containing L-L = dppm. These new $Co_2(CO)_4(L-$ L)-substituted alkyne compounds, 8-11, have been obtained by substitution reaction of carbonyl ligands, in the presence of Me₃NO, at the Co₂(CO)₆ units of 4-7 (see Scheme 1). The FT-IR spectral changes of these reactions were monitored until the $\nu_{\rm CO}$ bands of the parent complex had disappeared. In a similar manner, we have proceeded to obtain the very unstable green solid disubstituted-cobalt-alkvne compound 15 from icosa-9,11-diyne $(3)^{14}$ (see Scheme 2). On the other hand, the related complexes 12-14 were isolated, together with the wellknown $[Co_2(CO)_4(\mu-L-L)\{\mu_2-\eta^2-Me_3SiC_2\}]_2(C\equiv C)_2$ (L-L = dppm¹⁵ or dmpm¹⁶), from a Pd-catalyzed coupling reaction between $[Co_2(CO)_4(\mu-L-L)\{\mu_2-\eta^2-SiMe_3C_2\}](C\equiv CH)$ (L-L = dppm,¹⁵ dmpm¹⁶) and 4,4'- diiodoazobenzene, in 2:1 ratio. The mixture of products, in these reactions, was separated by TLC silica plates using hexane/CH2Cl2 (4:3) as eluent (see Scheme 2). All these compounds have been fully characterized by spectroscopic data (IR, UV-vis, ${}^{1}H$, ${}^{13}C{}^{1}H$, and ${}^{31}P{}^{1}H$) NMR, and MS) and elemental analysis, details of which are given in the Experimental Section.

Co(CO)₂

Me

(16)

(CH₂)₇-CH₃

The IR spectra of $Co_2(CO)_6$ -substituted alkyne complexes $(C_{2\nu}$ symmetry) exhibit four medium to strong absorptions in the carbonyl stretching region (at ca. 2089, 2054, 2030, and 2025 cm⁻¹). As expected, in phosphine-substituted alkyne complexes these absorptions lie at lower frequencies (2024-1969 cm⁻¹ for 8–13 with L-L= dppm and 2014–1953 cm⁻¹ for 14 with L-L= dmpm) because of the donor character of the ligands, and the spectral patterns are similar to those observed for previously reported cobalt-alkyne and cobalt-substitutedalkyne complexes.¹⁵⁻²² Complexes 4, 8, and 12-14 contain uncomplexed C \equiv C triple bonds, which display a $\nu_{C \equiv C}$ weak



Figure 1. ORTEP diagram of 9.

absorption between 2160 and 2145 cm^{-1} that could not be observed in 6 or 10.

All NMR data are consistent with the overall geometry established in the solid state for 9 (Figure 1) and with the proposed structures (Schemes 1 and 2). ¹H and ¹³C{¹H} NMR data are summarized in Tables 1 and 2. The ¹H NMR spectra of 1 and 2 prior to irradiation consist of two doublets of intensity 4 at ca. 7.85 ppm, corresponding to the 2 and 2' protons, and at ca. 7.55 ppm for the 3 and 3' protons. The ${}^{1}\text{H}$ NMR spectrum of the *cis*-form is expected to contain a set of signals similar in pattern to that of the trans-form, but with different chemical shifts. Under laser irradiation two new doublets are observed, and both ¹H resonances move significantly upfield (ca. 7.3 and 6.7 ppm), which suggests that the planar *cis* configuration leads to increased π -electron density in the rings. The ¹H NMR spectra of 4, 5, 8, 9, and 12– 14 show, as expected, that the $-SiMe_3$ is greatly affected by the coordination of " $Co_2(CO)_6$ " or " $Co_2(CO)_4(L-L)$ " units to an adjacent $-C \equiv C-$ group. In fact, the SiMe₃ resonance is shifted from 0.27 ppm, in the free ligand, to about 0.40 ppm, owing to the loss of C \equiv C triple-bond character.²³ In 4–14, the azobenzene proton signals are consistent with the incorporation of one or two $Co_2(CO)_6$ or $Co_2(CO)_4(L-L)$ units and appear as apparent doublets (AA'XX' system) in the aromatic compound range (7.0-8.0 ppm). They are easily identified because of their symmetry (they are mirror images) (Table 1). The phosphine phenyl rings protons are also observed in this range. It can be observed that in the ¹H NMR spectra of 10–13

the diasterotopic protons of the P-CH₂-P group are coupled with the two P atoms, giving two double triplet signals with $J_{\rm HH}$ and J_{PH} around 13.2 and 10.4 Hz, respectively. These resonances can also be observed in 14 (L-L = dmpm) with similar coupling constant values for $J_{\rm HH}$ and $J_{\rm PH}$. The ${}^{13}{\rm C}{}^{1}{\rm H}{}$ NMR chemical shifts of the carbonyl ligands bonded to the Co₂ units, in all complexes, appear as one or two signals at around δ 199 ppm or δ 202 and 207 ppm, which indicates a fast interchange on the NMR scale. The resonances of the free and coordinated acetylene units were easily observed, and the chemical shifts of their carbon atoms are in the range of analogous complexes (δ 80–105 ppm).^{15,16,18,22,24} Azobenzene carbon resonances appear between δ 120 and 155 ppm. The chemical shift for the C_4 atom in 4, 6, 8, and 10 is found to be very sensitive to cobalt complexation on the adjacent alkyne and shows a significant downfield shift (from 126 to 142 or 149 ppm) when they become 5, 7, 9, and 11 (Table 2). For disubstituted-cobalt-azobenzene-decyne complexes, 7 and 11, the carbon resonances due to the carbon chains, $-(CH_2)_7$ -CH₃, confirm the chemical equivalence in these molecules, whereas in the analogous monosubstituted-cobalt-azobenzenedecyne complexes, 6 and 10, different carbon resonances for both chains are observed for each of them (see the Experimental Section). The ${}^{13}C{}^{1}H{}$ NMR spectrum of 15 shows the resonances due to the coordinated carbon atoms in addition to those of the carbon chains, and, in the same manner as 7 and 11, the chemical equivalence of the molecule is demonstrated. The unambiguous assignments of all carbon

Table 3. Selected Bond Distances	(Å) and Angles (deg) for 9
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N(1)-N(1)#1	1.263(6)
C(4)–N(1)	1.418(5)
Co(1)-Co(2)	2.4631(7)
C(11)-C(12)	1.338(5)
C(12)–Si(1)	1.837(4)
C(1)-C(11)	1.456(5)
Co(1)-C(11)	1.955(4)
Co(2)-C(11)	1.975(3)
N(1)#1-N(1)-C(4)	114.4(4)
C(3)-C(4)-N(1)	123.8(3)
C(2)-C(3)-C(4)	119.8(4)
C(3)-C(2)-C(1)	121.2(3)
C(2)-C(1)-C(11)	120.6(3)
C(12)-C(11)-C(1)	139.9(3)
C(5)-C(4)-N(1)	116.4(3)
C(6) - C(5) - C(4)	120.8(4)
C(5)-C(6)-C(1)	120.2(4)
C(6)-C(1)-C(11)	121.2(3)
C(11)-C(12)-Si(1)	146.3(3)
C(6)-C(1)-C(11)-C(12)	62.8(6)
C(2)-C(1)-C(11)-C(12)	-117.7(5)

1.978(4)

1.963(4)

1.831(4)

1.831(4)

1.827(4)

1.827(4)

1.825(4)

1.820(4)

Article

atoms have been carried out by using homonuclear and heteronuclear two-dimensional correlation spectroscopy experiments and by comparison with analogous compounds.^{15,16,18,22,24} The room-temperature ³¹P{¹H} NMR spectra in CDCl₃ present a broad singlet that is shifted to higher frequencies (ca. 36 and 13 ppm for dppm and dmpm complexes, respectively) with respect to that of the free phosphine ligand because of the coordination. The positive FAB mass spectra of the substituted-cobalt alkyne complexes show the respective molecular ion or M⁺ – CO, as well as peaks corresponding to the loss of CO ligands.

Description of the Crystal and Molecular Structure of 9. A single-crystal X-ray diffraction study was performed on complex **9**. This study serves the obvious purpose of confirming the structure presented in Scheme 1. Figure 1 presents a molecular diagram of **9**, and the selected geometric parameters for this compound have been summarized in Table 3.

Compound 9 crystallizes with three CH_2Cl_2 molecules in the monoclinic crystal system, space group P2(1)/c (Table S1). Its crystal structure consists of discrete monomeric molecules of $[{SiMe_3(Co_2(CO)_4dppm)C_2}_2{(1,4-C_6H_4)N}_2]$ in *trans*-form. The acetylenic moieties are coordinated to $Co_2(CO)_4dppm$ fragments in each case. The " Co_2C_2 " core adopts a pseudotetrahedral geometry, and each of the cobalt atoms is also coordinated to two terminal carbonyl ligands and to the phosphorus atom from the dppm ligand.

The bond length N–N#1 found in 9 is 1.263(6) Å, similar to those reported in $C_6H_5C \equiv CC_6H_4N = NC_6H_4C \equiv CC_6H_5$ (1.264(5) Å),²⁵ (C_6H_5)₄ $C_6HC_6H_4N = NC_6H_4HC_6(C_6H_5)_4$ (1.263(3) Å),²⁵ (CH_3)₃SiC $\equiv CC_6H_4N = NC_6H_4C \equiv CSi$ (CH_3)₃ (1.230(5) Å),²⁶ {[$Co_2(CO)_6(\mu$ -HC $\equiv C$)] $C_6H_4N = \}_2$ (1.240(5) Å),²⁷ HC $\equiv CC_6H_4N = NC_6H_4C \equiv CH$ (1.247(2) Å),²⁷ and $H_3CC_6H_4N = NC_6H_4CH_3$ (1.251(2) Å).²⁸

The interatomic distance of Co(1)-Co(2), at 2.4631(7) Å, falls within the normal range for a Co–Co single bond²⁷ and is similar to Co–Co lengths observed for other dicobalt systems that are bridged by alkyne ligands.^{16,27,29,30}

The C(11)-C(12) length, 1.338(5) Å, lies in the range 1.33–1.36 Å reported for the alkylenic C–C bond in related

dicobalt complexes.^{16,27,29,30} This C–C distance shows a lengthening of ca. 0.15 Å from the value of 1.192(4) Å found in $(CH_3)_3$ Si C=CC₆H₄N=NC₆H₄C=CSi(CH₃)₃,²⁶ and this reflects the loss of triple-bond character as a result of coordination of the acetylenic moieties to the Co₂ units. The change in hybridization at C(11)–C(12) is also reflected in the angles C(12)–C(11)–C(1), 139.9(3)°, and C(11)–C(12)–Si(1), 146.3(3)°. The bridging ethynyl ligands are twisted out of the plane of the aryl group. The relevant torsion angles are C(6)–C(1)–C(11)–C(12), 62.8(6)°, and C(2)–C(1)–C(11)–C(12), -C(11)–C(12), -C(12)–C(11)–C(12), -117.7(5)°.

Co(1)-C(12)Co(2)-C(12)

C(16) - P(1)

C(16) - P(2)

C(17) - P(1)

C(23) - P(1)

C(29) - P(2)

C(35) - P(2)

The Co-C distances in the "Co₂C₂" core of **9** range from 1.955(4) to 1.978(4) Å, and these distances do not show an asymmetry pattern as observed in $[{Co₂(CO)₆(H C \equiv C)}_2(C_6H_4)]^{29}$ and in $[Co_2(CO)_4(\mu$ -dppm)]_2(\mu-\eta^2-HC_2(C \equiv C)_2C_2H).¹⁶

The average P–C distance of the bridging dppm ligands, 1.826(4) Å, is normal. 31

The bond angle of N(1)#1–N(1)–C(4) is 114.4(4)° and indicates that the two nitrogen atoms exist at almost sp² hybridization. The angles C(3)–C(4)–N(1) and C(5)–C(4)–N(1) are 123.8(3)° and 116.4(3)°, respectively.

Electrochemical Study. Table 4 assembles potential values for the reduction and oxidation of compounds 1, 2, and 4-13 in CH₂Cl₂ solution. All values are referred to the Fc^{*+}/Fc^{*} system.

The electrochemical reductions of **1** and **2** render two distinct waves in both cases (Figure 2). The first (less negative) ones at $E_{1/2} = -1.03$ and -1.13 V are chemically and electrochemically reversible either at room temperature or at -30 °C. The more negative waves at $E_{1/2} = -1.52$ and -1.70 V are chemically quasi-reversible. Reduction potentials are more negative for **2**, as a consequence of the higher electron-donating nature of the decynyl tails. Positive scans until the limit allowed by the solvent system (ca. +1.6 V) did not show any voltammetric oxidation peaks.

Compounds 4–7, containing one (4 and 6) or two (5 and 7) $C_2Co_2(CO)_6$ redox centers, lead to quite similar voltammetric responses. Positive oxidation sweeps show, in all cases, only one

Table 4. $E_{1/2}$ Values for Compounds 1, 2, and $4-13^a$

	reduction							
	$\begin{array}{c} E_{1/2} \\ C_2 \text{Co}_2(\text{CO})_6 \end{array}$	$E_{1/2}$ azob 1	$E_{1/2}$ azob 2	$\begin{array}{c} E_{1/2} \\ C_2 \text{Co}_2(\text{CO})_6 \text{dppm} \end{array}$	$\begin{array}{c} E_{1/2}\\ C_2 Co_2 \end{array}$			
1		-1.03	-1.52					
2		-1.13	-1.70					
4	-0.95	-1.07	-1.66		1.23			
5	-0.95	-1.08	-1.64		1.23			
6	-1.01	-1.12	-1.71		1.19			
7	-0.98	-1.14	-1.76		1.18			
8		-1.08	-1.50	-1.63	0.73			
9		-1.15	n.d. ^b	-1.61	0.73			
10		-1.17	-1.60	-1.72	0.66			
11		-1.19	-1.55	-1.74	0.65			
12		-1.04	n.d.	-1.58	0.76			
13		-1.02	n.d.	-1.57	0.76			





Figure 2. Cyclic and square wave voltammograms for the reduction of a solution of **1** in CH₂Cl₂ containing 0.15 M TBAPF₆ at 25 °C on a Pt working electrode. CV: $\nu = 0.1$ V s⁻¹; SWV: scan increment = 2 mV, SW amplitude = 25 mV, frequency = 30 Hz.

peak, which is irreversible at 25 °C but turns chemically reversible at -30 °C ($E_{1/2}$ around 1.20 V). Thus, the losses of one (4 and 6) or two (5 and 7) electrons produce cations that decompose in solution, but these homogeneous reactions are slow enough so that CV reversible waves can be observed at -30 °C.

In the reduction sweeps of 4-7, two very close and irreversible (at 25 $^{\circ}$ C) peaks are obtained at ca. -1 V. When the temperature is decreased to -30 °C, the corresponding anodic peaks can be observed for both processes, but complete chemical reversibility is not attained. The potential values for these peaks (see Table 4) indicate that one of them should be assigned to an azobenzene-group-centered reduction, while the other should involve reductions centered in the $Co_2(CO)_6$ units (which always appear at potentials near -1 V, with small differences due to the environment of the cluster).^{18,24b,c,32} Both processes are so close in potential that it is quite difficult to ensure which of the redox centers corresponds to each of the reductions in 4-7. However, if we take into account that the $C_2Co_2(CO)_6$ -cluster-centered reduction corresponds to the gain of one and two electrons per molecule for 4, 6 and 5, 7, respectively (analogous to the oxidation processes), while the reduction centered in the azobenzene ligand involves just one electron per molecule in all compounds, the intensity difference between both peaks (better observed in SWV, Figure 3) indicates that the less negative process is $C_2Co_2(CO)_6$ -centered and the more negative one is azobenzene-centered.

Figure 3. Square wave voltammograms for the reduction and oxidation of solutions of 4 and 5 in CH_2Cl_2 containing 0.15 M TBAPF₆ at -30 °C on a glassy carbon working electrode. Scan increment = 2 mV, SW amplitude = 25 mV, frequency = 30 Hz.

The voltammetric oxidation sweep of compounds 5 and 7, with a single bielectronic wave (and not two consecutive monoelectronic ones), indicates that no electronic communication between the two equivalent $C_2Co_2(CO)_6$ units through the azobenzene bridge can be appreciated by electrochemical means.

Compounds 8–13 contain $C_2Co_2(CO)_4(dppm)$ redox centers. Substitution of two CO ligands by electron-donating dppm makes the redox centers much easier to oxidize and more difficult to reduce than in 4–7. Also, bidentate dppm stabilizes cations and anions that are now much more resistant to chemical decomposition in solution in the time scale of the electrochemical cyclic and square wave voltammetry (CV and SWV, respectively) experiments.³³

Electrochemical oxidation of 8–13 leads to a completely chemically reversible wave (even at room temperature) appearing at $E_{1/2}$ in the 0.65 to 0.76 V range (see Table 4 and Figures 4 and 5) and corresponding to the loss of electrons from the C₂Co₂(CO)₄(dppm) clusters. The wave is mono-

Figure 4. Cyclic voltammograms for the reduction and oxidation of a solution of 8 in CH_2Cl_2 containing 0.15 M TBAPF₆ at -30 °C on a glassy carbon working electrode at v = 0.1 V s⁻¹.

Figure 5. Cyclic voltammograms for the reduction and oxidation of a solution of 9 in CH₂Cl₂ containing 0.15 M TBAPF₆ at -30 °C on a glassy carbon working electrode at $\nu = 0.1$ V s⁻¹.

electronic for 8, 10, and 12 and bielectronic for 9, 11, and 13. The appearance of a single bielectronic wave for the oxidation of 9, 11, and 13 (containing two equivalent redox centers) indicates that no significant electronic communication between both centers through the azobenzene ligand can be appreciated. The easier oxidation observed for 10 and 11 agrees with the more electron donating nature of the organic chain, as also observed above for the free ligand 2.

When sweeping to negative potentials, a monoelectronic and completely reversible wave, between -1.02 and -1.19 V, appears for 8-13 (Table 4, Figures 4 and 5). The characteristics and potential of this peak allow to assign it unambiguously to an azobenzene-centered reduction. The electron-donating $C_2Co_2(CO)_4(dppm)$ group shifts the reduction of the azobenzene group toward potentials more negative than for the free ligands 1 and 2. This fact is observed with 8 and 10, but is most evident with 9 and 11, containing two such donating clusters. However, with compounds 12 and 13, the intermediate -CC- groups somewhat shield the cluster effect. When the sweep is extended to even more negative potentials, some of the compounds show a wave at around -1.55 V, which is chemically quasi-reversible and can be assigned to a second reduction centered in the azobenzene ligand. This wave is clearly distinguished for 8, 10, and 11 (Figure 4), but is partly masked in the remaining compounds by a further reduction process, between -1.57 and -1.74 V, which is completely chemically reversible at low temperature and whose peak current is equivalent to that of the oxidation process described above (Figure 5). This process corresponds to $C_2Co_2(CO)_4(dppm)$ -centered reductions.^{18,24b,c,33}

Compound 15 is closely related to those studied by Duffy et al.³² At room temperature, reduction renders a single completely irreversible peak at 1.07 V, as the anion readily decomposes in solution. However, at -30 °C, the homogeneous decomposition is slow enough so that two waves, the first one chemically reversible and the second one quasi-reversible, are observed at $E_{1/2} = -0.99$ and -1.26 V ($\Delta E_{1/2} = 270$ mV). Correspondingly, two quasi-reversible waves are observed in the oxidation of 15 at rt (+1.24 and +1.53 V), the first one chemically reversible at -30 °C. $\Delta E_{1/2} = 290$ mV agrees well with the reduction result and with related compounds³² and shows that significant electronic communication takes place between both redox centers through the carbon bridge,³³ as expected.

Electronic Absorption Spectra. The UV-vis spectra of *trans*-azobenzene derivatives 1, 2, and 9–13 (Table 5) show three well-separated absorption bands:^{3,34} the lowest energy and much weaker one corresponds to the parity-forbidden $n \rightarrow \pi^*$ transition at ca. 445 nm ($\varepsilon = 90 \text{ M}^{-1} \text{ cm}^{-1}$) for the organic ligands and at ca. 472 nm for compounds containing a

	$\pi \rightarrow \pi^*$ (nm) ε	$n \rightarrow \pi^* (nm)$	$\Phi \rightarrow \Phi^* (nm)$	$\sigma \rightarrow \sigma^* (nm)$	MLCT (nm)
	$(M^{-1} cm^{-1})$	$\varepsilon(\mathrm{M}^{-1}~\mathrm{cm}^{-1})$	$\varepsilon(\mathrm{M}^{-1}~\mathrm{cm}^{-1})$	$\varepsilon(\mathrm{M}^{-1}~\mathrm{cm}^{-1})$	$\varepsilon(\mathrm{M}^{-1}~\mathrm{cm}^{-1})$
trans-Cpd					
1	368	442	249		
	1600	80	980		
2	369	446	246		
	3090	160	1320		
L-12 ^{<i>a</i>}	350	457	258		
	2300	230	4300		
L-13 ^a	371	468	258		
	2100	660	4190		
9	382			471	238
	17 618			17 800	51 680
11	334 sh		271 sh	472	236
				24 860	87 140
12	342 sh			378	235
				2060	5300
13	376			474	237
	2230			2120	6156
cis-Cpd					
1	268	447	253		
	1030	100	1000		
2	267	450	255		
	1390	210	1346		

Table 5. Electronic Spectral Data and Transition Assignments of Azobenzene Derivative Compounds in DCM

^{*a*}L-12 1-[(C \equiv C)C₂SiMe₃]-1'-(I)[(1,4-C₆H₄)N]₂ and L-13 1,1'-[(C \equiv C)C₂SiMe₃]₂[(1,4-C₆H₄)N]₂.

Figure 6. ¹H NMR spectra of 1 (a) before UV light irradiation and (b) after UV light irradiation.

 $C_2Co_2(CO)_4(dppm)$ unit; the strong UV band at ca. 370 nm ($\varepsilon = 1600 \text{ M}^{-1} \text{ cm}^{-1}$) arises from the symmetry-allowed $\pi \to \pi^*$ transition; the highest energy band at ca. 240 nm ($\varepsilon = 700 \text{ M}^{-1} \text{ cm}^{-1}$) is due to a $\Phi \to \Phi^*$ transition. This may be considered as localized in the rings, because of the close association of the Φ orbitals with the benzene rings. In addition, the electronic spectra of compounds 9–13 present the $\sigma \to \sigma^*$ transition of the Co–Co bond at ca. 474 nm and the intense MLCT band at ca. 335 nm. In the *cis*-azobenzene compounds 1 and 2 while the n $\to \pi^*$ transition is slightly more intense and appears at similar wavelengths, the $\pi \to \pi^*$ transition is weaker and appears at higher energy, ca. 235 nm ($\varepsilon = 750 \text{ M}^{-1} \text{ cm}^{-1}$). The marked difference between the *trans*- and *cis*-isomers is due to the nonplanar configuration of the *cis*-form.

Photochemical *trans*-to-*cis* and Thermal *cis*-to-*trans* Isomerizations. Isomerization kinetics of 1 and 2 were investigated in dichloromethane (DCM). Excitation in the $\pi \rightarrow \pi^*$ transition leads to an overall *trans*-to-*cis* isomerization, while reverse *cis*-to-*trans* isomerization can be induced either thermally or photochemically by excitation in the $n \rightarrow \pi^*$ transition. The rate constants, of both process, were determined by monitoring the decreasing or increasing absorbance of the *trans*- $\pi \rightarrow \pi^*$ or *cis*- $\pi \rightarrow \pi^*$ transition (Table S2).

Figure S79 shows typical absorbance changes during *trans*-to*cis* isomerization of 1 as a function of 365 nm light irradiation time. Under irradiation the intensity of the absorption peak at 368 nm gradually decreases until an equilibrium state is reached. At the same time, a new peak at 268 nm gradually increases and the weaker peak at 447 nm becomes a little more pronounced. Similar behavior was also observed for compound **2**. A reverse *cis*-to-*trans* reaction is induced thermally, and the rate constants for the thermal isomerization of **1** and **2** are summarized in Table S2.

Both processes follow a first-order reaction according to the kinetic equation

$$\ln[(A_0 - A_\infty)/(A_t - A_\infty)] = kt$$

where A_0 , A_v and A_∞ are the initial absorbance, absorbance at time *t*, and absorbance at the photostationary state; *k* is the isomerization rate constant.

The presence of clear isosbestic points during the course of the reactions confirms that a transition between only the *cis* and the *trans* species is taking place.

Isomerization is further evidenced by ¹H NMR spectra of the solutions, which clearly show that changes in UV–vis spectra can be correlated to NMR peaks attributed to the *trans*- and *cis*-forms of compounds 1 and 2 (Figure 6).

The isomerization rate constants of 2 are much lower than that of 1 (Figure S80), and the half-life time is about twice higher (Table S2). Photo- and thermal isomerization become more difficult due to the steric hindrance effect of the decyne groups.

The experimental rate constants of cobalt complex isomerization processes could not be calculated, because of the decomposition of the organometallic complex under UV irradiation to give rise to a free organic ligand.

Undertaking a comparative study with other azobenzene derivatives^{12c,35} has not been possible because of the different experimental conditions.

Mesomorphic Properties of 2. Compounds 8, 9, 10, and 11 do not exhibit mesomorphic behavior. However, compound 2 shows a monotropic liquid-crystalline phase with a nematic

mesophase. This mesophase is investigated by polarized optical microscopy studies (POM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) (see the SI).

The nematic phase is monotropic, which means that the mesophase is thermodynamically unstable, and, therefore, it only appears in the cooling process, due to hysteresis in the crystallization. Mesophase identification was achieved by polarized microscopy, with a magnification of 20×. The polarizing optical microscopy images show a typical nematic Schlieren texture 36,37 when compound **2** is cooling down from the isotropic liquid at 10 °C/min. The nematic droplets began to form a nematic texture (Figure 7), but finally, when the

Figure 7. Polarizing optical photomicrograph ($20\times$) of **2** obtained at 37 °C on cooling from the isotropic liquid.

temperature was reduced to 35.3 °C, a crystalline texture is formed. On the other hand, the thermogravimetric analysis showed that the mesogen begins to decompose at 260 °C. The DSC traces of 2 do not exhibit a nematic phase on heating, but they reveal a narrow nematic phase on cooling. On the first heating, compound 2 melts to a isotropic liquid at 52.5 °C (ΔH = 176 kJ mol⁻¹), and on the first cooling, it enters a nematic phase at 38.2 °C (ΔH = 13 kJ mol⁻¹) and a crystalline phase at 32.0 °C (ΔH = 151 kJ mol⁻¹), with a short mesophase range of ΔT = 6.18 °C. The difference in these transition enthalpies is due to the fact that a larger energy is considered necessary to interrupt both the positional and the orientational order of the crystalline phase, while less energy is required to interrupt the orientational order of the nematic phase.

CONCLUSION

Organic ligands have been synthesized from coupling reactions of 4,4'-diiodoazobenzene with TMSA or 1-decyne, under Sonogashira coupling conditions. *para*-Alkynyl azobenzene derivatives (R-Azo-R) and their organometallic cobalt complexes linked to the azobenzene unit by a π -conjugated carbon bridge have been synthesized in satisfactory yields by direct reaction between Co₂(CO)₈ and the organic ligands. Complexes containing Co₂(CO)₄(L-L) have been obtained by substitution reaction of carbonyl ligands, in the presence of Me₃NO.

Photochemical and thermal *trans*-to-*cis* and *cis*-to-*trans* isomerization processes have been studied for organic ligands. The rate constants show obvious dependence on the molecular

structure of azobenzene and, thus, for 2 are much lower because of the higher steric effects.

EXPERIMENTAL SECTION

General Considerations. All reactions and manipulations were routinely carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free Ar. All solvents for synthetic use were dried and distilled under argon by standard procedures³⁸ and bubbled with Ar for 1 h after distillation and before use. The reactions were monitored by IR spectroscopy, ¹H NMR, and TLC, and the products were characterized by IR, ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR, DEPT, COSY, HMBC, HMQC, UVvis, elemental analyses, and mass spectrometry. Column chromatography was performed by using silica gel (60 mesh, 40-63 Å) (Fluka) and preparative TLC on 20×20 cm glass plates coated with silica gel (SDS 60-17 μ m, 0.25 mm thick). Trimethylsililacetylene, PdCl₂(PPh₃)₂, Co₂(CO)₈, and PPh₃ (Fluka) and 1,2-bis-(diphenylphosphino)methane (dppm), CuI, 4,4'-diiodoazobenzene, hexafluorophosphate of tetrabutylamonium, and 1-decyne (Aldrich) were used as received. Trimethylamine N-oxide (Aldrich) was sublimed prior to use and stored under Ar. Compounds [(SiMe₃C \equiv C)(1,4-C₆H₄)N]₂ (1)³⁹ and [Co₂(CO)₄(μ -L-L)(μ_2 - η^2 -SiMe₃C₂)](C \equiv CH) (L-L = dppm¹⁵ or dmpm¹⁶) were prepared according to the literature. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra and HMQC (heteronuclear multiple quantum correlation) and HMBC (heteronuclear multiple bond correlation) experiments were recorded on Bruker AMX-300 and Bruker DRX-500 instruments. Chemical shifts were measured relative to either an internal reference of tetramethylsilane or residual protons of the solvents. Infrared spectra were measured on a Nicolet 380 FT-IR spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the University Autónoma of Madrid on a PerkinElmer 240 B microanalyzer. Electronic spectra were recorded on a Unicam UV 2 UV-visible spectrophotometer, 10 mm quartz cells with a capacity of 3.5 cm³ were utilized for measurements, and initial concentrations of compounds were ca. 10⁻⁴ M. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB and EI by the Mass Laboratory of the University Autónoma of Madrid. Electrochemical measurements were carried out with an AUTOLAB 30 potentiostat/galvanostat. Cyclic and square wave voltammetry experiments were performed with a three-electrode cell under a N₂ (>99.9995%) atmosphere. A Pt-mesh counter electrode and an Ag-wire quasi-reference electrode were used. The working electrodes were either Pt or glassy carbon disks. Compounds were dissolved in dry CH₂Cl₂ containing 0.15 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. All potential values in this work are referred to the Fc*+/ Fc* (Fc* = decamethylferrocene) system, which was added as internal reference after each short series of measurements. $E_{1/2} = (E_{pa} + E_{pc})/2$ of the ferrocene/ferricinium couple (Fc⁺/Fc) was also measured as +0.55 V vs Fc*+/Fc* in the CH2Cl2 solution. Experiments were carried out at 25 °C and at -30 °C. For studying the liquid crystalline behavior, the optical textures of the mesophases were studied with a Nikon Eclipse LV 100 POL polarizing microscope equipped with a Linkam hot-stage and Linkam THMS 600 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a TA Instruments Q20 instrument operated at a scanning rate of 10 °C min⁻¹ on both heating and cooling. The apparatus was calibrated with indium (156.6 °C; 28.71 J g⁻¹) as the standard. TGA was carried out in a TGA-Q5000 apparatus at a heating rate of 10°/min under nitrogen up to 600 °C and under air from 600 to 750 °C.

 $[(SiMe_3C \equiv C)(1,4-C_6H_4)N]_2$ (1). To a solution of 4,4'-diiodoazobenzene (0.50 g, 1.15 mmol) in Et₃N (30 mL) was added, at room temperature (rt), 1.6 mL (1.10 g, 11.3 mmol) of TMSA in the presence of the PdCl₂(PPh₃)₂ catalyst (80.7 mg, 0.115 mmol), CuI (21.9 mg, 0.115 mmol), and PPh₃ (60.3 mg, 0.23 mmol). The resulting mixture was stirred at rt for 36 h. The reaction was monitored by thin-layer chromatography (TLC). The solvent was evaporated under reduced pressure, and the residue purified by chromatography on a hexane-packed silica column (200 g) using hexane/ CH_2Cl_2 (2:1) as eluent, to afford 1 (0.41 g, 95% yield) as a stable orange-red solid.

1: IR (CH₂Cl₂, cm⁻¹): 2155 vw (C=C). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.86 (d, J_{HH} = 8.7 Hz, 2H_{2,2}'); 7.60 (d, J_{HH} = 8.7 Hz, 2H_{3,3}'); 0.27 (s, 18H, 2 –SiMe₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 151.9 (s, 2C₁); 132.8 (s, 2C_{3,3}'); 126.1 (s, 2C₄); 122.9 (s, 2C_{2,2}'); 104.6 (s, 2C₉); 97.2 (s, 2C₁₀); -0.1 (s, 2 –SiMe₃). MS (EI⁺, m/z): 374.2 [M⁺]. Anal. Calcd for C₂₂H₂₆N₂Si₂ (374.6): C, 70.53; H, 7.00; N, 7.48. Found: C, 70.68; H, 7.23; N, 7.15.

 ${[CH_3-(CH_2)_{7^-}C \equiv C][(1,4-C_6H_4)N]}_2$ (2) and lcosa-9,11-diyne (3). To a solution of 4,4'-diiodoazobenzene (0.21 g, 0.48 mmol) in Et₃N (35 mL) and THF (10 mL) was added, at room temperature, 0.87 mL (0.667 g, 4.83 mmol) of 1-decyne in the presence of PdCl₂(PPh₃)₂ catalyst (33.7 mg, 0.048 mmol), CuI (9.14 mg, 0.048 mmol), and PPh₃ (25.18 mg, 0.096 mmol). The resulting mixture was stirred at rt for 60 h. The reaction was monitored by TLC. The solvent was evaporated under reduced pressure, and the residue purified by chromatography on a hexane-packed silica column (200 g) using hexane as eluent, to afford 2 (185 mg, 84% yield) as a stable orange solid in addition to the well-known icosa-9,11-diyne (3)¹⁴ and nonanoic acid, as byproducts.

2: ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.83 (d, $J_{\text{HH}} = 8.6$ Hz, 2H_{2,2'}); 7.51 (d, $J_{\text{HH}} = 8.6$ Hz, 2H_{3,3'}); 2.44 (t, $J_{\text{HH}} = 7.0$ Hz, 4H, 2 -CH₂-); 1.63 (q, $J_{\text{HH}} = 7.1$ Hz, 4H, 2 -CH₂-); 1.47 (m, 4H, 2 -CH₂-); 1.31 (m, 16H, 2 -(CH₂)₄-); 0.89 (t, $J_{\text{HH}} = 6.7$ Hz, 6H, 2 -CH₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 151.3 (s, 2C₁); 132.3 (s, 2C_{3,3'}); 127.0 (s, 2C₄); 122.8 (s, 2C_{2,2'}); 93.5 (s, 2C₉); 80.5 (s, 2C₁₀); 31.8 (s), 29.2 (s), 29.1 (s), 28.9 (s), 28.6 (s), 22.6 (s), and 19.6 (s) (14C, 2 -(CH₂)₇-); 14.1 (s, 2C, 2 -CH₃). MS (FAB⁺, m/z): 455.3 [M⁺]. Anal. Calcd for C₃₂H₄₂N₂ (454.7): C, 84.53; H, 9.31; N, 6.16. Found: C, 84.70; H, 9.40; N, 6.00.

1-[Co₂(CO)₆[μ_2 · η^2 -C₂SiMe₃]]-1'-(C≡CSiMe₃)][(1,4-C₆H₄)N]₂ (4) and 1,1'-[Co₂(CO)₆]{ μ_2 · η^2 -C₂SiMe₃]]₂[(1,4-C₆H₄)N]₂ (5). To a solution of 1 (0.40 g, 1.07 mmol) in CH₂Cl₂ (50 mL) was added 0.5 equiv of Co₂(CO)₈. The reaction mixture was monitored by FT-IR, ¹H NMR spectroscopy, and TLC until the signals of the parent compounds, 1 and Co₂(CO)₈, had disappeared. After stirring the mixture at room temperature for 26 h, the solvent was removed under vacuum and the residue was purified by TLC using hexane/CH₂Cl₂ (2:1) as eluent, to afford 4 (226 mg, 32% yield) and 5 (202 mg, 20% yield) as unstable reddish-brown solids. 5 has also been obtained as the only product in high yield (97%) from 1 and Co₂(CO)₈, in a ratio of 1:2, and subsequent chromatography with hexane/CH₂Cl₂ (2:1) on a silica column.

4: IR (CH₂Cl₂, cm⁻¹): 2159 vw (C \equiv C), 2088 m (CO), 2054 s (CO), 2027 vs (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.89 (d, *J*_{HH} = 8.7 Hz, H_{6,6}'); 7.86 (d, *J*_{HH} = 8.5 Hz, H_{2,2}'); 7.64 (d, *J*_{HH} = 8.7 Hz, H_{6,6}'); 7.86 (d, *J*_{HH} = 8.5 Hz, H_{2,2}'); 7.64 (d, *J*_{HH} = 8.7 Hz, H_{7,7}'); 7.60 (d, *J*_{HH} = 8.5 Hz, H_{3,3}'); 0.43 (s, 9H, -CSiMe₃); 0.28 (s, 9H, \equiv CSiMe₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 199.7 (s, CO); 152.1 (s, C₅); 151.8 (s, C₁); 142.1 (s, C₈); 132.9 (s, C_{3,3}'); 130.6 (s, C_{7,7}'); 125.9 (s, C₄); 123.6 (s, C_{6,6}'); 122.8 (s, C_{2,2}'); 104.7 (s, C₉); 103.7 (s, C₁₁); 97.3 (s, C₁₀); 80.3 (s, C₁₂); 0.91 (s, -CSiMe₃); -0.07 (s, \equiv CSiMe₃). MS (FAB⁺, *m*/*z*): 632.1 [M⁺ - CO]; 576.1 [M⁺ - 3CO]; 548.1 [M⁺ - 4CO]; 520.1 [M⁺ - 5CO]; 492.1 [M⁺ - 6CO].

5: IR (CH₂Cl₂, cm⁻¹): 2088 m (CO), 2053 s (CO), 2023 vs (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.90 (d, J_{HH} = 8.5 Hz, 2H_{6,6}'); 7.65 (d, J_{HH} = 8.5 Hz, 2H_{7,7}'); 0.43 (s, 18H, 2 –CSiMe₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 199.8 (s, CO); 152.0 (s, 2C₅); 142.0 (s, 2C₈); 130.7 (s, 2C_{7,7}'); 123.6 (s, 2C_{6,6}'); 103.8 (s, 2C₁₁); 80.3 (s, 2C₁₂); 0.92 (s, 2 –SiMe₃). MS (FAB⁺, *m*/*z*): 918.1 [M⁺ – CO]; 862.1 [M⁺ – 3CO]; 806.1 [M⁺ – 5CO].

1-[Co₂(CO)₆{μ₂-η²-C₂-(CH₂)₇-CH₃]]-1'-[CH₃-(CH₂)₇-C≡C][(1,4-C₆H₄)N]₂ (6) and 1,1'-[Co₂(CO)₆{μ₂-η²-C₂-(CH₂)₇-CH₃]]₂[(1,4-C₆H₄)N]₂ (7). To a solution of 2 (150 mg, 0.33 mmol) in CH₂Cl₂ (40 mL) was added 0.5 equiv of Co₂(CO)₈. The reaction mixture was monitored by FT-IR, ¹H NMR spectroscopy, and TLC until the signals of the parent compounds, **2** and Co₂(CO)₈, disappeared. After stirring the mixture at room temperature for 72 h, the solvent was removed under vacuum and the residue was purified by TLC using hexane/CH₂Cl₂ (3:1) as eluent, to afford **6** (85.5 mg, 35% yield) and 7 (77.9 mg, 23% yield) as unstable reddish-brown solids. 7 has also been obtained as an only product in high yield (89%) from 2 and $Co_2(CO)_{8^{j}}$ in a ratio of 1:2, and subsequent chromatography with hexane/CH₂Cl₂ (3:1) on a silica column.

6: IR (CH₂Cl₂, cm⁻¹): 2089 m (CO), 2053 vs (CO), 2028 vs (CO), 2022 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.89 (d, J_{HH} = 8.5 Hz, $H_{6,6'}$); 7.86 (d, J_{HH} = 8.6 Hz, $H_{2,2'}$); 7.62 (d, J_{HH} = 8.5 Hz, $H_{7,7'}$); 7.53 (d, $J_{\rm HH}$ = 8.5 Hz, $H_{3,3'}$); 3.08 (t, $J_{\rm HH}$ = 8.0 Hz, 4H, 2 -CH₂-); 2.45 (t, $J_{\rm HH}$ = 7.0 Hz, 4H, 2 –CH₂–); 1.77 (q, $J_{\rm HH}$ = 7.6 Hz, 4H, 2 $-CH_2-$; 1.64 (q, $J_{HH} = 7.2$ Hz, 4H, 2 $-CH_2-$); 1.49 (q, $J_{HH} = 7.3$ Hz, 4H, 2 -CH₂-); 1.30 (m, 8H, 2 -(CH₂)₂-); 0.90 (t, J_{HH} = 7.0 Hz, 3H, $-CH_3$); 0.89 (t, $J_{HH} = 6.6$ Hz, 3H, $-CH_3$). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 199.6 (s, CO); 151.7 (s, C₅); 151.5 (s, C₁); 142.0 (s, C_8); 132.4 (s, $C_{3,3'}$); 129.9 (s, $C_{7,7'}$); 127.1 (s, C_4); 123.5 (s, $C_{6,6'}$); 122.8 (s, $C_{2,2'}$); 100.7 (s, C_{11}); 93.6 (s, C_9); 89.7 (s, C_{12}); 80.5 (s, C₁₀); 34.3 (s, C), 32.0 (s, C), 31.9 (s, C), 31.8 (s, C), 29.7 (s, C), 29.4 (s, C), 29.2 (s, 2C), 29.1 (s, C), 29.0 (s, C), 28.7 (s, C), 22.7 (s, C), 22.6 (s, C), and 19.6 (s, C) (14C, 2 -(CH₂)₇-); 14.2 (s, -CH₃); 14.1 $(s_1 - CH_3)$. MS (FAB⁺, m/z): 741.0 [M⁺]; 712.0 [M⁺ - CO]; 656.0 $[M^{+} - 3CO]$; 628.0 $[M^{+} - 4CO]$; 600.0 $[M^{+} - 5CO]$; 573.0 $[M^{+} -$ 6CO]

7: IR (CH₂Cl₂, cm⁻¹): 2089 m (CO), 2053 vs (CO), 2029 vs (CO), 2023 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.91 (d, J_{HH} = 8.4 Hz, 2H₆₆'); 7.63 (d, J_{HH} = 8.4 Hz, 2H₇₇'); 3.00 (t, J_{HH} = 8.0 Hz, 4H, 2 –CH₂–); 1.69 (q, J_{HH} = 7.6 Hz, 4H, 2 –CH₂–); 1.45 (q, J_{HH} = 7.4 Hz, 4H, 2 –CH₂–); 1.32 (m, 4H, 2 –CH₂–); 1.22 (m, 12H, 2 –(CH₂)₃–); 0.82 (t, J_{HH} = 6.8 Hz, 6H, 2 –CH₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 199.5 (s, CO); 151.8 (s, 2C₅); 142.1 (s, 2C₈); 129.9 (s, 2C₇₇'); 123.4 (s, 2C₆₆'); 100.8 (s, 2C₁₁); 89.7 (s, 2C₁₂); 34.3 (s, 2C), 32.0 (s, 2C), 31.8 (s, 2C), 29.7 (s, 2C), 29.4 (s, 2C), 29.2 (s, 2C) and 22.7 (s, 2C) (14C, 2 –(CH₂)₇–); 14.1 (s, 2C, 2 –CH₃). MS (FAB⁺, *m*/z): 1026.5 [M⁺]; 914.5 [M⁺ – 4CO]; 802.5 [M⁺ – 8CO]; 746.5 [M⁺ – 10CO].

 $1-[Co_2(CO)_4(\mu-dppm){\mu_2-\eta^2-C_2SiMe_3}]-1'-(C \equiv CSiMe_3)[(1,4-C_6H_4)N]_2$ (8). A solution of 4 (41 mg, 0.062 mmol) and 0.062 mmol of dppm in CH₂Cl₂ (50 mL) was prepared. Trimethylamine *N*-oxide (13.8 mg, 0.124 mmol) was added, and the reaction mixture, monitored by FT-IR, was stirred at 40 °C for 24 h. The reaction was stopped when all the starting material had been consumed. After removal of solvent under vacuum, the residue was purified by TLC using hexane/CH₂Cl₂ (2:1) as eluent, to afford 8 (56.4 mg, 92% yield) as a stable reddish-brown solid.

8: IR (CH₂Cl₂, cm⁻¹): 2155 vw (C≡C), 2019 s (CO), 1994 vs (CO), 1966 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.89 (d, $J_{\rm HH}$ = 8.6 Hz, H_{2,2'}); 7.73 (d, $J_{\rm HH}$ = 8.5 Hz, H_{6,6'}); 7.63 (d, $J_{\rm HH}$ = 8.6 Hz, $H_{3,3'}$); 7.25 (d, J_{HH} = 8.5 Hz, $H_{7,7'}$); 7.30–7.08 (m, 12H), (8H, m-Ph), (4H, p-Ph); 6.99 (t, $J_{\rm HH}$ = 7.4 Hz, 8H, o-Ph); 3.36–3.27 (m, 2H, P-CH₂-P); 0.37 (s, 9H, −CSiMe₃); 0.29 (s, 9H, ≡CSiMe₃). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 34.8 (s br, 2P, P-CH₂-P). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 207.3 (m, CO); 202.8 (m, CO); 152.3 (s, C₁); 150.6 (s, C₅); 148.9 (s, C₈); 138.7 (t, J_{CP} = 24.4 Hz, *i*-Ph); 134.5 (t, J_{CP} = 16.6 Hz, *i*-Ph); 132.9 (s, $C_{3,3'}$); 132.7 (t, J_{CP} = 6.5 Hz, *o*-Ph); 130.4 (s, $C_{7,7'}$); 130.3 (t, J_{CP} = 5.9 Hz, *o*-Ph); 129.7 (s, *p*-Ph); 129.2 (s, *p*-Ph); 129 Ph); 128.5 (t, $J_{CP} = 4.7$ Hz, m-Ph); 127.9 (t, $J_{CP} = 4.7$ Hz, m-Ph); 125.4 (s, C₄); 123.1 (s, C_{6,6'}); 122.7 (s, C_{2,2'}); 104.8 (s, C₉); 104.7 (t, $J_{CP} = 7.5$ Hz, C_{11}); 97.0 (s, C_{10}); 90.1 (t, $J_{CP} = 10.0$ Hz, C_{12}); 35.7 (t, $J_{CP} = 20.6 \text{ Hz}, \text{ P-CH}_2\text{-P}); 0.89 \text{ (s, -CSiMe}_3); -0.03 \text{ (s, =CSiMe}_3).$ MS (FAB⁺, m/z): 989.2 [M⁺]; 961.2 [M⁺ - CO]; 933.2 [M⁺ -2CO; 905.2 [M⁺ - 3CO]; 877.2 [M⁺ - 4CO].

 $1,1'-[Co_2(CO)_4(\mu-dppm){\mu_2-\eta^2-C_2SiMe_3}]_2[(1,4-C_6H_4)N]_2$ (9). The procedure described above was used, but with 5 (115 mg, 0.12 mmol), dppm (0.24 mmol), and trimethylamine N-oxide (0.48 mmol) as reactants. A stable reddish-brown solid was obtained (185 mg, 95% yield).

9: IR (CH₂Cl₂, cm⁻¹): 2017 s (CO), 1991 vs (CO), 1966 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.69 (d, J_{HH} = 8.1 Hz, 2H_{6,6}'); 7.21 (d, J_{HH} = 8.3 Hz, 2H_{7,7}'); 7.24–7.03 (m, 24H) (16H, *m*-Ph), (8H, *p*-Ph); 6.93 (t, J_{HH} = 7.5 Hz, 16H, *o*-Ph); 3.30 (m, 2H, 2 P-CH₂-P); 3.25 (m, 2H, 2 P-CH₂-P); 0.38 (s, 18H, 2 –CSiMe₃). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 34.9 (s br, 4P, 2 P-CH₂-P). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 207.3 (m, CO); 202.8 (m, CO); 150.9 (s, 2C₅); 147.9 (s, 2C₈); 138.8 (t, J_{CP} = 24.3 Hz, *i*-Ph); 134.6 (t, J_{CP} = 16.5 Hz, *i*-Ph); 132.7 (t, J_{CP} = 6.4 Hz, *o*-Ph); 130.5 (s, 2C_{7,7}); 130.4 (t, J_{CP} = 5.9 Hz, *o*-Ph); 129.7 (s, *p*-Ph); 129.2 (s, *p*-Ph); 128.5 (t, J_{CP} = 4.7 Hz, *m*-Ph); 127.9 (t, J_{CP} = 4.7 Hz, *m*-Ph); 122.9 (s, 2C₆₆·); 104.8 (t, J_{CP} = 7.4 Hz, 2C₁₁); 89.8 (t, J_{CP} = 10.0 Hz, 2C₁₂); 35.7 (t, J_{CP} = 20.6 Hz, 2 P-CH₂-P); 0.94 (s, 2 -CSiMe₃). MS (FAB⁺, *m*/*z*): 1603.1 [M⁺]; 1575.1 [M⁺ - CO]; 1547.1 [M⁺ - 2CO]; 1519.1 [M⁺ - 3CO]; 1463.1 [M⁺ - 5CO]; 1435.1 [M⁺ - 6CO]; 1407.1 [M⁺ - 7CO]; 1379.1 [M⁺ - 8CO].

1-[Co₂(CO)₄(μ -dppm){ μ_2 - η^2 -C₂-(CH₂)₇-CH₃]]-1'-[CH₃-(CH₂)₇-C≡C]-[(1,4-C₆H₄)N]₂ (**10**). A solution of **6** (50.0 mg, 0.0675 mmol) and 0.0675 mmol of dppm in CH₂Cl₂ (50 mL) was prepared. Trimethylamine N-oxide (15.0 mg, 0.135 mmol) was added, and the reaction mixture, monitored by FT-IR, was stirred at 45 °C for 48 h. The reaction was stopped when all the starting material had been consumed. After removal of the solvent under vacuum, the residue was purified by TLC using hexane/CH₂Cl₂ (3:2) as eluent, to afford **10** (64.2 mg, 89% yield) as a stable dark red solid.

10: IR (CH₂Cl₂, cm⁻¹): 2024 s (CO), 1998 vs (CO), 1974 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.86 (d, J_{HH} = 8.5 Hz, $H_{2,2'}$); 7.75 (d, $J_{\rm HH}$ = 8.5 Hz, $H_{6.6'}$); 7.53 (d, $J_{\rm HH}$ = 8.5 Hz, $H_{3.3'}$); 7.33 (d, $J_{\rm HH}$ = 8.5 Hz, H_{7.7}); 7.30-7.20 (m, 12H), (8H, m-Ph), (4H, p-Ph); 7.17 $(t, J_{HH} = 7.0 \text{ Hz}, 4\text{H}, o\text{-Ph}); 7.08 (t, J_{HH} = 7.3 \text{ Hz}, 4\text{H}, o\text{-Ph}); 3.28 (dt, J_{HH} = 7.0 \text{ Hz}, 3\text{Hz}, 3\text{H$ $J_{\rm HH}$ = 13.1 Hz, $J_{\rm PH}$ = 10.3 Hz, 1H, ABXY, P-CH₂-P); 3.16 (dt, $J_{\rm HH}$ = 13.0 Hz, J_{PH} = 10.5 Hz, 1H, ABXY, P-CH₂-P); 3.05-2.96 (m, 2H, $-CH_2-$); 2.45 (t, $J_{HH} = 7.0$ Hz, 2H, $-CH_2-$); 1.73–1.60 (m, 4H, 2 $-CH_2-$); 1.52-1.45 (m, 2H, $-CH_2-$); 1.32-1.23 (m, 18H, 9 $-CH_2-$); 0.90 (t, $J_{HH} = 6.7$ Hz, 3H, $-CH_3$); 0.86 (t, $J_{HH} = 6.7$ Hz, 3H, -CH₃). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 37.7 (s br, 2P, P-CH₂-P). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 206.1 (m, CO); 202.2 (m, CO); 151.7 (s, C_1); 150.4 (s, C_5); 148.5 (s, C_8); 138.0 (t, $J_{CP} = 22.2$ Hz, *i*-Ph); 135.5 (i, J_{CP} = 17.5 Hz, *i*-Ph); 132.3 (s, $C_{3,3'}$); 132.2 (t, J_{CP} = 6.5 Hz, o-Ph); 130.8 (t, J_{CP} = 6.1 Hz, o-Ph); 129.7 (s, p-Ph); 129.5 (s, $C_{7.7'}$; 129.2 (s, p-Ph); 128.3 (t, J_{CP} = 4.6 Hz, m-Ph); 128.0 (t, J_{CP} = 4.7 Hz, m-Ph); 126.5 (s, C_4); 123.0 (s, $C_{6.6'}$); 122.6 (s, $C_{2.2'}$); 105.5 (m, C_{11}); 93.2 (s, C_9); 92.5 (t, J_{CP} = 8.2 Hz, C_{12}); 80.6 (s, C_{10}); 35.7 (s, C); 35.6 (m, P-CH₂-P); 31.86 (s, C), 31.85 (s, C), 31.6 (t, $J_{CP} = 2.5$ Hz, C), 29.9 (s, C), 29.4 (s, C), 29.3 (s, C), 29.2 (s, C), 29.1 (s, C), 29.0 (s, C), 28.7 (s, C), 22.68 (s, C), 22.66 (s, C), and 19.6 (s, C) $(14C, 2 - (CH_2)_7 -); 14.12 (s, -CH_3); 14.09 (s, -CH_3). MS (FAB^+, -CH_3)$ m/z): 1041.0 [M⁺ - CO]; 957.0 [M⁺ - 4CO].

1,1'-[$Co_2(CO)_4(\mu$ -dppm){ μ_2 - η^2 - C_2 -(CH_2) $_7$ - CH_3]] $_2[(1,4-C_6H_4)N]_2$ (11). The procedure described above was used, but with 7 (50.3 mg, 0.049 mmol), dppm (0.098 mmol), and trimethylamine *N*-oxide (0.196 mmol) as reactants. A stable reddish-brown solid was obtained (70.9 mg, 86% yield).

11: IR (CH₂Cl₂, cm⁻¹): 2022 s (CO), 1997 vs (CO), 1973 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.76 (d, J_{HH} = 8.4 Hz, 2H_{6,6'}); 7.32 (d, $J_{\rm HH}$ = 8.4 Hz, $2H_{7,7'}$); 7.28–7.18 (m, 28H), (16H, o-Ph), (8H, *m*-Ph), (4H, *p*-Ph); 7.15 (t, J_{HH} = 7.4 Hz, 4H, *p*-Ph); 7.06 (t, J_{HH} = 7.4 Hz, 8H, *m*-Ph); 3.27 (dt, J_{HH} = 13.0 Hz, J_{PH} = 10.3 Hz, 2H, ABXY, 2 P-CH₂-P); 3.17 (dt, J_{HH} = 13.0 Hz, J_{PH} = 10.4 Hz, 2H, ABXY, 2 P- CH_2 -P); 3.02–2.97 (m, 4H, 2 – CH_2 -); 1.69–1.66 (m, 4H, 2 -CH₂-); 1.37-1.33 (m, 4H, 2 -CH₂-); 1.26-1.22 (m, 16H, 8 $-CH_2$ -); 0.85 (t, J_{HH} = 7.0 Hz, 6H, 2 $-CH_3$). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 37.7 (s br, 4P, 2 P-CH₂-P). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 206.2 (m, CO); 204.1 (m, CO); 150.8 (s, 2C₅); 147.7 (s, $2C_8$); 138.0 (t, $J_{CP} = 22.2$ Hz, *i*-Ph); 135.6 (t, $J_{CP} = 17.5$ Hz, *i*-Ph); 132.3 (t, $J_{CP} = 6.4$ Hz, o-Ph); 130.9 (t, $J_{CP} = 6.1$ Hz, o-Ph); 129.8 (s, 2C_{7,7'}); 129.6 (s, *p*-Ph); 129.3 (s, *p*-Ph); 128.4 (t, *J*_{CP} = 4.6 Hz, *m*-Ph); 128.1 (t, $J_{CP} = 4.7$ Hz, m-Ph); 122.9 (s, $2C_{6,6'}$); 105.9 (m, $2C_{11}$); 92.7 (m, 2C₁₂); 35.8 (s, 2C); 35.7 (m, 2 P-CH₂-P); 31.9 (s, 2C), 31.7 (s, 2C), 30.0 (s, 2C), 29.5 (s, 2C), 29.3 (s, 2C), and 22.7 (s, 2C) (14C, 2 $-(CH_2)_7-$; 14.1 (s, 2C, 2 $-CH_3$). MS (FAB⁺, m/z): 1655.4 [M⁺ -CO]; 1627.4 [M⁺ - 2CO]; 1571.4 [M⁺ - 4CO]; 1543.4 [M⁺ -5CO]; 1515.4 [M⁺ - 6CO]; 1459.4 [M⁺ - 8CO].

 $\begin{array}{l} 1-[Co_{2}(CO)_{4}(\mu-dppm)\{\mu_{2}-\eta^{2}-(C\equiv C)C_{2}SiMe_{3}]]-1'-(I)[(1,4-C_{6}H_{4})N]_{2}\\ (12) \quad and \quad 1,1'-[Co_{2}(CO)_{4}(\mu-dppm)\{\mu_{2}-\eta^{2}-(C\equiv C)C_{2}SiMe_{3}\}]_{2}[(1,4-C_{6}H_{4})N]_{2} \quad (13). \text{ To a solution of } 4,4'-diiodoazobenzene \quad (82.0 mg, 0.19 mmol) in Et_{3}N \quad (30 mL) were added, under stirring and cooling at \\ \end{array}$

0 °C, PdCl₂(PPh₃)₂ (13.3 mg, 0.019 mmol), CuI (3.6 mg, 0.019 mmol), PPh₃ (10.0 mg, 0.038 mmol), and $[Co_2(CO)_4(\mu$ -dppm)(μ_2 - η^2 -SiMe₃C₂)](C==CH)¹⁵ (0.28 g, 0.38 mmol). After 30 min, the reaction mixture was progressively warmed to room temperature and stirred for 72 h. After the solvent was removed under vacuum, the residue was extracted with CH₂Cl₂ and purified by TLC using hexane/CH₂Cl₂ (4:3) as eluent, to afford **12** (band 1) (79.2 mg, 40% yield) and **13** (band 3) (62.7 mg, 20% yield) as stable reddish-brown solids in addition to $[Co_2(CO)_4(\mu$ -dppm){ μ_2 - η^2 -SiMe₃C₂}]₂(C==C)₂ (band 2), whose spectroscopy data are already reported in and are consistent with the compound described above.¹⁵

12: IR (CH_2Cl_2, cm^{-1}) : 2155 vw $(C \equiv C)$, 2020 s (CO), 1993 vs (CO), 1965 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.90 (d, $J_{\rm HH}$ = 8.5 Hz, H_{6,6}'); 7.88 (d, $J_{\rm HH}$ = 8.6 Hz, H_{3,3}'); 7.68 (d, $J_{\rm HH}$ = 8.6 Hz, $H_{2,2'}$); 7.46 (d, $J_{HH} = 8.5$ Hz, $H_{7,7'}$); 7.31–7.19 (m, 12H), (8H, m-Ph), (4H, p-Ph); 7.14–7.09 (m, 8H, o-Ph); 3.96 (dt, J_{HH} = 13.3 Hz, $J_{\rm PH}$ = 10.9 Hz, 1H, ABXY, P-CH₂-P); 3.32 (dt, $J_{\rm HH}$ = 13.0 Hz, $J_{\rm PH}$ = 10.1 Hz, 1H, ABXY, P-CH₂-P); 0.41 (s, 9H, -CSiMe₃). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 37.3 (s br, 2P, P-CH₂-P). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 207.0 (m, CO); 201.6 (m, CO); 152.1 (s, C₁); 150.9 (s, C₅); 138.5 (s, C_{3,3'}); 137.8 (m, *i*-Ph); 137.7 (m, *i*-Ph); 134.5 (m, *i*-Ph); 134.4 (m, *i*-Ph); 132.7 (t, $J_{CP} = 6.5$ Hz, *o*-Ph); 132.6 (t, J_{CP} = 6.4 Hz, o-Ph); 131.8 (s, $C_{7.7'}$); 131.1 (t, J_{CP} = 6.0 Hz, o-Ph); 131.0 (t, $J_{CP} = 6.0$ Hz, o-Ph); 129.9 (s, p-Ph); 129.8 (s, p-Ph); 129.4 (s, p-Ph); 129.3 (s, p-Ph); 128.4 (t, J_{CP} = 4.8 Hz, m-Ph); 128.3 (t, J_{CP} = 3.7 Hz, *m*-Ph); 128.2 (t, $J_{CP} = 4.9$ Hz, *m*-Ph); 128.1 (t, $J_{CP} = 4.8$ Hz, *m*-Ph); 124.5 (s, C_{2,2'}); 123.2 (s, C_{6,6'}); 97.8 (s, C₄); 96.9 (s, C₈); 94.7 (s, C_{10} ; 90.5 (m, C_{11}); 82.4 (s, C_9); 76.7 (m, C_{12}); 37.8 (t, J_{CP} = 20.2 Hz; P-CH₂-P); 0.59 (s, $-CSiMe_3$). MS (FAB⁺, m/z): 1013.7 [M⁺ - CO]; $957.7 [M^+ - 3CO]; 929.7 [M^+ - 4CO].$

13: IR (CH₂Cl₂, cm⁻¹): 2145 vw (C≡C), 2023 s (CO), 1998 vs (CO), 1975 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.99 (d, $J_{\text{HH}} = 8.4$ Hz, 2H₆₆'); 7.54 (d, $J_{\text{HH}} = 8.4$ Hz, 2H₇₇'); 7.50–7.26 (m, 24H), (16H, *m*-Ph), (8H, *p*-Ph); 7.24–7.15 (m, 16H, *o*-Ph); 4.02 (dt, $J_{\text{HH}} = 13.4$ Hz, $J_{\text{PH}} = 10.7$ Hz, 2H, ABXY, 2 P-CH₂-P); 3.38 (dt, $J_{\text{HH}} = 13.4$ Hz, $J_{\text{PH}} = 10.1$ Hz, 2H, ABXY, 2 P-CH₂-P); 0.47 (s, 18H, 2 –CSiMe₃). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 37.3 (s br, 4P, 2 P-CH₂-P). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 207.1 (m, CO); 201.7 (m, CO); 151.3 (s, 2C₅); 137.8 (t, $J_{\text{CP}} = 23.2$ Hz, *i*-Ph); 134.5 (t, $J_{\text{CP}} = 17.7$ Hz, *i*-Ph); 132.6 (t, $J_{\text{CP}} = 6.4$ Hz, *o*-Ph); 131.8 (s, 2C₇₇'); 131.1 (t, $J_{\text{CP}} = 6.1$ Hz, *o*-Ph); 129.9 (s, *p*-Ph); 129.4 (s, *p*-Ph); 128.4 (t, $J_{\text{CP}} = 4.7$ Hz, *m*-Ph); 128.2 (t, $J_{\text{CP}} = 4.8$ Hz, *m*-Ph); 123.1 (s, 2C₆₆'); 96.8 (s, 2C₈); 94.8 (s, 2C₁₀); 90.7 (m, 2C₁₁); 82.9 (s, 2C₉); 76.6 (m, 2C₁₂); 37.8 (t, $J_{\text{CP}} = 20.1$, 2 P-CH₂-P); 0.60 (s, 2 –CSiMe₃). MS (FAB⁺, *m*/z): 1651.9 [M⁺]; 1623.9 [M⁺ – CO]; 1567.9 [M⁺ – 3CO]; 1539.9 [M⁺ – 4CO]; 1511.9 [M⁺ – 5CO]; 1483.9 [M⁺ – 6CO]; 1455.9 [M⁺ – 7CO]; 1427.9 [M⁺ – 8CO].

 $\begin{array}{l} 1-[Co_{2}(CO)_{4}(\mu-dmpm)\{\mu_{2}-\eta^{2}-(C\equiv C)C_{2}SiMe_{3}]]-1'-(l)[(1,4-C_{6}H_{4})N]_{2}\\ (14). The procedure described above was used from 4,4'-diiodoazobenzene (18.0 mg, 0.041 mmol), PdCl_{2}(PPh_{3})_{2} (10\% mmol), CuI (10\% mmol), and PPh_{3} (20\% mmol), but with <math>[Co_{2}(CO)_{4}(\mu-dmpm)(\mu_{2}-\eta^{2}-SiMe_{3}C_{2})](C\equiv CH)^{16}$ (40.5 mg, 0.082 mmol) as terminal alkyne. 14 was obtained as a stable reddish-brown solid in 25% yield in addition to $[Co_{2}(CO)_{4}(\mu-dmpm)\{\mu_{2}-\eta^{2}-SiMe_{3}C_{2}\}]_{2}(C\equiv C)_{2}$, whose spectroscopy data are already reported in and are consistent with the compound described above.¹⁶

14: IR (CH₂Cl₂, cm⁻¹): 2152 vw (C=C), 2014 s (CO), 1985 vs (CO), 1953 s (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.91 (d, $J_{\text{HH}} = 8.5$ Hz, 4H, H_{6,6}', H_{3,3}'); 7.69 (d, $J_{\text{HH}} = 8.6$ Hz, H_{2,2}'); 7.54 (d, $J_{\text{HH}} = 8.5$ Hz, H_{7,7}'); 2.78 (dt, $J_{\text{HH}} = 13.5$ Hz, $J_{\text{PH}} = 10.0$ Hz, 1H, ABXY, P-CH₂-P); 2.17 (dt, $J_{\text{HH}} = 13.6$ Hz, $J_{\text{PH}} = 10.1$ Hz, 1H, ABXY, P-CH₂-P); 1.58 (m, 12H, Me_2 P-CH₂-PMe₂); 0.36 (s, 9H, -CSiMe₃). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 13.7 (s br, 2P, P-CH₂-P). MS (FAB⁺, m/z): 793.8 [M⁺]; 765.8 [M⁺ - CO]; 737.8 [M⁺ - 2CO]; 709.8 [M⁺ - 3CO]; 681.8 [M⁺ - 4CO].

 $[Co_2(CO)_6[\mu_2-\eta^2-C_2-(CH_2)_7-CH_3]]_2$ (15). To a solution of icosa-9,11diyne (3) (111.0 mg, 0.406 mmol) in hexane (50 mL) was added $Co_2(CO)_8$ (277.9 mg, 0.812 mmol), and the reaction mixture was stirred at room temperature for 24 h. The reaction was monitored by FT-IR and ¹H NMR spectroscopy until the signals of the parent compounds had disappeared. After the solvent was removed under vacuum, the residue was extracted with hexane/CH₂Cl₂ (5:1) and purified by TLC using hexane/CH₂Cl₂ (3:1) as eluent, to afford **15** (337.0 mg, 98% yield) as a unstable dark red solid.

15: IR (CH_2Cl_2, cm^{-1}) : 2060 s (CO), 2006 vs (CO), 1960 sh (CO). ¹H NMR (300 MHz, CDCl₃, ppm): δ 2.88 (m, 4H, 2 – CH₂–); 1.79 (q, J_{HH} = 7.7 Hz, 4H, 2 – CH₂–); 1.57 (q, J_{HH} = 7.2 Hz, 4H, 2 – CH₂–); 1.35 (m, 4H, 2 – CH₂–); 1.31 (m, 12H, 2 – (CH₂)₃–); 0.94 (m, 6H, 2 – CH₃). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 199.4 (s, CO); 106.8 (s, 2C) and 91.8 (s, 2C) (4C_{cord}); 33.5 (s, 2C), 31.9 (s, 2C), 31.8 (s, 2C), 29.6 (s, 2C), 29.4 (s, 2C), 29.2 (s, 2C), and 22.6 (s, 2C) (14C, 2 – (CH₂)₇–); 14.1 (s, 2C, 2 – CH₃).

 $[Co_2(CO)_4(\mu-dmpm){\mu_2-\eta^2-C_2-(CH_2)_7-CH_3}]_2$ (**16**). A solution of **15** (100 mg, 0.114 mmol) and 0.011 mmol of dmpm in CH₂Cl₂ (50 mL) was prepared. Trimethylamine *N*-oxide (34.3 mg, 0.456 mmol) was added, and the reaction mixture, monitored by FTIR, was stirred at room temperature for 10 days. The reaction was stopped when all the starting material had been consumed. After removal of the solvent under vacuum, the residue was extracted with CH₂Cl₂ and purified by TLC using hexane/CH₂Cl₂ (2:1) as eluent, to afford **16** (25 mg, 21% yield) as a very unstable green-red solid.

16: IR (CH₂Cl₂, cm⁻¹): 2020 s (CO), 2007 vs (CO), 1970 s (CO). **X-ray Crystallography.** Red crystals of **9** were grown by slow evaporation of the solvent from a solution of the compound in CH₂Cl₂ solvent at room temperature. A summary of selected crystallographic data for **9** is given in Table S1. A red single crystal of approximate dimensions 0.15 × 0.10 × 0.05 mm with prismatic shape was mounted on a glass fiber and transferred to a Bruker SMART 6K CCD areadetector three-circle diffractometer with a MAC Science Co., Ltd. rotating anode (Cu Kα radiation, $\lambda = 1.541$ 78 Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA.⁴⁰ X-ray data were collected at 100 K, with a combination of six runs at different φ and 2 θ angles, 3600 frames.

The raw intensity data frames were integrated with the SAINT program,⁴¹ which also applied corrections for Lorentz and polarization effects.

The substantial redundancy in data allows empirical absorption corrections (SADABS)⁴² to be applied using multiple measurements of symmetry-equivalent reflections.

The software package SHELXTL version 6.10^{43} was used for space group determination, structure solution, and refinement. The structure was solved by direct methods (SHELXS-97),⁴⁴ completed with difference Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97,⁴⁵ minimizing $\omega(F_o^2 - F_c^2)^2$. Weighted *R* factors (R_w) and all goodness of fit *S* are based on F^2 ; conventional *R* factors (R) are based on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. The hydrogen atom positions for the complex **9** were calculated geometrically and were allowed to ride on their parent carbon atoms with fixed isotropic *U*.

Final positional parameters, anisotropic thermal parameters, hydrogen atom parameters, and structure amplitudes are available as Supporting Information. CCDC-1047086 (9) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/products/csd/request.

ASSOCIATED CONTENT

Supporting Information

CIF files giving further details of the crystal structure determination for compounds **9**, including bond lengths, bond angles, and anisotropic and isotropic displacement parameters, as well as all other analytical data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00257.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Support for this work is acknowledged from the Comunidad de Madrid (FOTOCARBON-CM S2013/MIT-2841), Spain. Thanks to Joaquín Barberá Gracia (Universidad de Zaragoza, Spain) for technical and scientific support.

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