Electronic Communication in $[Co_2(CO)_6]_2$-Diyne and $[Co_2(CO)_4(dppm)]_2$-Diyne Complexes

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The electrochemical behaviour of the $[Co_2(CO)_6]_2(\mu\text{-R–C≡C–L–C≡C–R})$ and $[Co_2(CO)_4(dppm)]_2(\mu\text{-R–C≡C–L–C≡C–R})$ series is reported. Qualitative evidence suggests that both through-space and through-bond interactions are operating with different relative weight depending on the spacer L.

Introduction

Organometallic polymers with unsaturated bridging units are currently the subject of much research because of their potential as non-linear optical (NLO) materials[1][2], liquid crystals[3][4], and quasi-one-dimensional conductors[5]. The properties of such materials can be tuned by varying the organic link or by adjusting the metal itself. Poly-yne segments are recognised to allow long-distance electronic interactions through π-delocalization[6][7][8][9][10][11][12]. Several studies have been performed on organometallic "rigid rod" polymers, Lapinte[13] and Gladysz[14] have demonstrated that conjugated C_2 to C_{20} σ-acetylide bridges constitute the most efficient link between organometallic redox-active termini. Recently, we have investigated the electronic communication between redox-active clusters joined with diynes in a σ/π fashion[15][16][17], although this kind of interaction is suspected to reduce the π-conjugation.

Electrochemistry represents a simple tool to evaluate the extent of the electronic interaction between two redox centres[18][19][20][21]. When there is no electronic interaction between two redox cores, the $E°'$ values differ only by a small statistical factor[22] (ca. 36 mV at 298 K) and in polarography/CV a single wave/peak is observed. On the other hand, when there is charge delocalization over the two centres, the $E°'$ values for the redox processes differ up to about 700 mV[23], giving two, more or less resolved, waves/peaks.

In this paper, we study a large series of complexes where the redox centres are either "$Co_2(CO)_6$" or "$Co_2(CO)_4$(dppm)" moieties and the bidentate ligand is a μ-R−C≡C−L−C≡C−R chain[15][16][24]. The "Co_2-alkyne" electrochemical reduction is reasonably well understood[24][25], although fast ECE processes complicate its behaviour. Phosphane ligand substitution in $Co_2(CO)_6$(μ-alkyne) has been extensively studied mainly by Robinson et al.[26][27][28][29][30][31] The $Co_2(CO)_{6-n}(PR_3)_n$(alkyne) series exhibits a further electrochemically and chemically reversible 1e oxidation[24] only when n = 3, 4 and R = OMe. Similar behaviour has recently been observed for $Co_2(CO)_4$(dppm)(μ-alkyne) derivatives[32].

Results and Discussion

Complexes $[Co_2(CO)_6]_2$(μ-diyne) have been synthesised by reaction of $Co_2(CO)_8$ with the appropriate ligand[33] (Figure 1).

The subsequent CO substitution was achieved by thermal reaction of the $[Co_2(CO)_6]_2$(μ-diyne) with dppm [bis(diphenylphosphanyl)methane, $Ph_2P-CH_2-PPh_2$][34] (Scheme 1).

Scheme 1

$$2\,Co_2(CO)_8 + R-C{\equiv}C-L-C{\equiv}C-R \rightarrow [Co_2(CO)_6]_2(R-C{\equiv}C-L-C{\equiv}C-R) + 4\,CO$$

$$[Co_2(CO)_6]_2(R-C{\equiv}C-L-C{\equiv}C-R) + 2\,Ph_2P-CH_2-PPh_2 \rightarrow [Co_2(CO)_4(Ph_2P-CH_2-PPh_2)]_2(R-C{\equiv}C-L-C{\equiv}C-R) + 4\,CO$$

In most cases, in order to increase the yields of the desired compounds, $Co_2(CO)_6$(dppm) was employed as starting reagent[35].

Scheme 2

$$Co_2(CO)_8 + Ph_2P-CH_2-PPh_2 \rightarrow Co_2(CO)_6(Ph_2P-CH_2-PPh_2) + 2\,CO$$

$$2\,Co_2(CO)_6(Ph_2P-CH_2-PPh_2) + (R-C{\equiv}C-L-C{\equiv}C-R) \rightarrow [Co_2(CO)_4(Ph_2P-CH_2-PPh_2)]_2(R-C{\equiv}C-L-C{\equiv}C-R) + 4\,CO$$

Some substituted complexes were not stable enough to be isolated from both the pathways, namely $[Co_2(CO)_4(dppm)]_2(H-C{\equiv}C-CH_2-CH_2-C{\equiv}C-H)$, $[Co_2(CO)_4(dppm)]_2(H_3C-C{\equiv}C-C{\equiv}C-CH_3)$, and $[Co_2(CO)_4(dppm)]_2[Me_3Si-C{\equiv}C-C{\equiv}C-SiMe_3]$.

At room temperature, all diyne complexes **1**−**10** undergo an *apparently* single two-electron reduction process in the relative CV responses. However, as the temperature is low-

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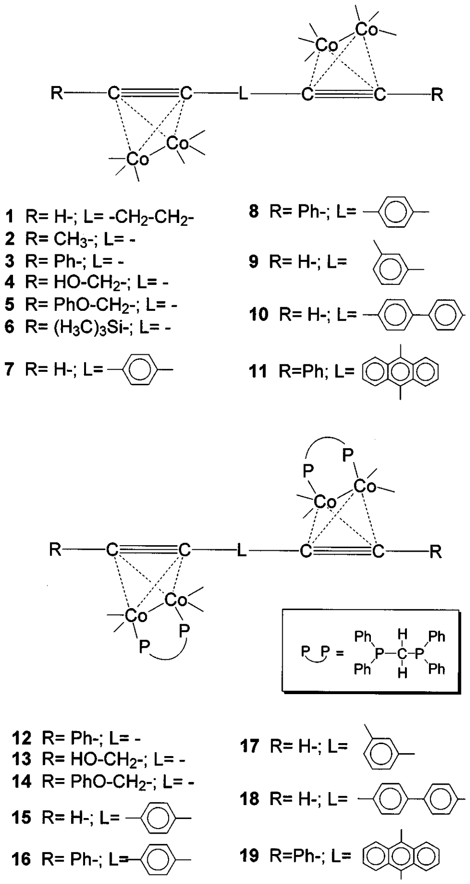
Figure 1. Sketch of structures of complexes **1**−**19**; CO ligands are omitted for clarity

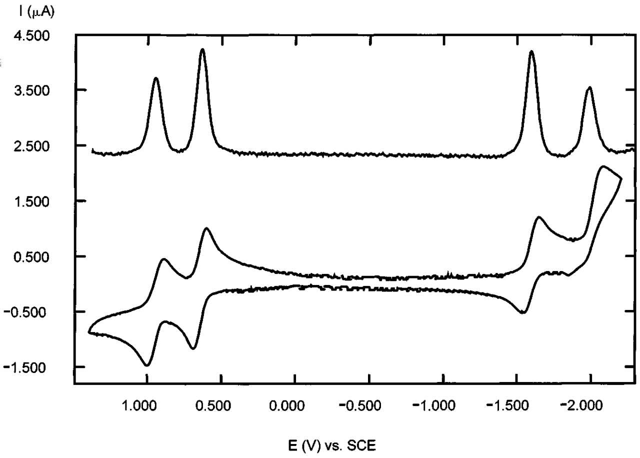


ered and/or the scan rate is increased, the chemical complications involving the primary radical anions are quenched so that two peak couples, corresponding to subsequent 1e reductions and showing full chemical reversibility, are observed[16][17].

For complexes **1**−**6**, two distinct peak couples are clearly observed in CV, at −30°C, allowing the calculation of the relevant formal electrode potentials $E^{\circ\prime}$ as $(E_p{}^c + E_p{}^a)/2$ (Table 1). Generally speaking, the external substituents R of the diyne affect the half-life of the electrogenerated monoanion; hydrogen substituents, in particular, give faster decomposition: in every case such complications can be eliminated by further raising the scan rate.

The complexes $[Co_2(CO)_4(dppm)]_2(R-C{\equiv}C-L-C{\equiv}C-R)$ (**12**−**19**) are interesting molecules as they have two identical redox centres which can undergo both reduction and oxidation processes. At ambient temperature, the cathodic scans mirror those of the parent compounds, albeit with a higher degree of chemical reversibility; the study of their $\Delta E^{\circ\prime}$ values requires low temperature. In contrast, two peak couples corresponding to Nernstian and chemically reversible 1e oxidation processes are always observed in the anodic region (Figure 2). It is worth mentioning that at low temperature (−30°C) such oxidation processes become electrochemically quasi-reversible, as testified by the increased ΔE_p values.

Figure 2. Electrochemical response of a THF solution of **12** ($1 \cdot 10^{-3}$ M) on a GC electrode at room temperature: SWV at 30 Hz (top) and CV at 0.2 V s^{-1}(bottom)



Certainly, the presence of dppm, which allows reversible oxidations to be observed at room temperature, facilitates the experimental work and, furthermore, permits the evaluation of the electronic communication for compounds such as **19**, where the aromatic 9,10-bis(phenylethynyl)anthracene gives reduction processes which overlap with those of the redox centres under study. In fact, no indication of electronic interaction could be obtained for **11**[17].

For complexes **7**−**10** and **15**−**19**, where the aromatic spacer is interpolated between the "Co_2C_2" moieties, the $E^{\circ\prime}$ values cannot be immediately evaluated from the CV responses at low temperature since the peaks are partially overlapped. We successfully employed a computer-assisted technique for peak resolution enhancement called *semi-derivative voltammetry*[36][37], where the CV data are first semi-integrated and then differentiated with respect to time (Figure 3). Alternatively, we used the Square Wave Voltammetry (SWV) technique[38] to resolve this overlapping. The relevant $E^{\circ\prime}$ values obtained from the above described techniques are in agreement (±10 mV) and are reported in Table 1.

For all compounds **1**−**19** the $\Delta E^{\circ\prime}$ values suggest a low to moderate electronic communication between the two bimetallic cores (formally corresponding to class-II mixed-valence systems in the Hush-Robin-Day formulation)[39][40].

Through-Bond and Through-Space Electronic Interaction

A large amount of data have been published on the metal−metal interactions in binuclear complexes M−L−M′ evaluated by electrochemistry. However, there are only rare attempts to rationalise this collection of potentials by using the distinction between through-space and through-bond interaction. Although both represent approximations, they can be distinguished via specially designed models. Through-space is the solvent-dependent coulombic interaction within the molecule and through-bond is both the so-called inductive (by successive polarisation of the bonds)

Figure 3. Cyclic voltammograms (top) and corresponding semiderivative voltammograms (bottom) of a THF solution of **16** on a GC electrode at 0.2 V s^{-1}; the cathodic scan is recorded at −30°C, the anodic scan at room temperature; Fc* = decamethylferrocene, added as an internal standard

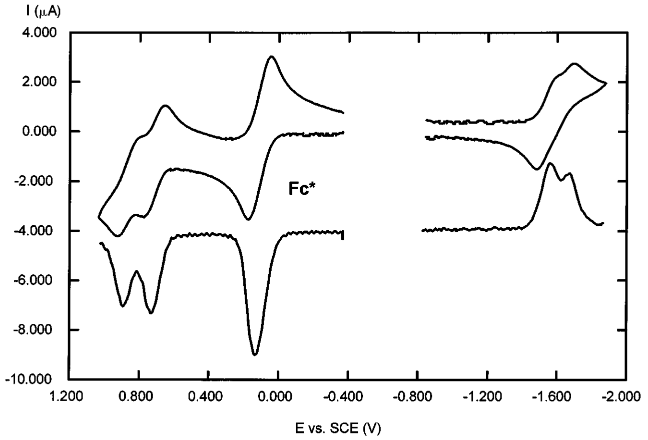


Table 1. Electrochemical data for complexes **1−11**, evaluated in THF containing $[Bu_4N][PF_6]$ (0.1 M) at −30°C, GC working electrode

Complex	$E^{\circ\prime}$(0,0/0,1−) [V vs. SCE]	$E^{\circ\prime}$(0,1−/1−,1−) [V vs. SCE]	$\Delta E^{\circ\prime}$ [mV]
1	−0.96	−1.11	150
2	−0.81	−1.27	460
3	−0.80	−1.20	400
4	−0.83	−1.16	330
5	−0.79	−1.20	410
6	−0.80	−1.28	480
7	−0.91	−1.02	110
8	−0.87	−1.01	140
9	−0.93	−1.07	140
10	−0.93	−1.01	80
11	[a]	[a]	[a]

[a] Not evaluated because of overlapping of the reduction of the 9,10-bis(phenylethynyl)anthracene.

and mesomeric (delocalised) effects[41]. It seems to be generally true that extensive intervening π-bond systems facilitate electron communication while σ-bond networks help less. However, a σ-bond system is strongly preferable to transmission across free space.

Complex **1**, having a $-CH_2-CH_2-$ spacer (a region of saturation), shows a $\Delta E^{\circ\prime}$ value about three times lower than those of complexes **2−6** but similar to those of complexes **7−9** where a phenylene spacer is present (Table 1). This comparison suggests that through-space interaction may be operative in complex **1**, especially if one considers that the $-CH_2-CH_2-$ chain is flexible enough to allow the two redox "Co_2C_2" centres to be in close contact.

In a simple electrostatic model the dependence of comproportionation constant K_c on the distance between the redox centres has been discussed by Reimers and Hush[42]; ln K_c, and hence $\Delta E^{\circ\prime}$[22][43][44][45], is found to be inversely related to both the distance between the redox centres and the dielectric constant (ε) of the solvent. On passing from THF (ε = 7.5) to acetone (ε = 21.0) to acetonitrile (ε = 36.6), $\Delta E^{\circ\prime}$ of compound **1** has decreasing values of 150, 90, and 50 mV, respectively. Although ion pairing effects play a role especially in the presence of supporting electrolyte in high concentration (0.1 M $[NBu_4][PF_6]$), the trend is consistent with this view[*]. The general tendency for the remaining **2−10** complexes is as follows: (i) compounds **2−6** (having a direct C−C bond between the two subunits) show a weaker dependence of $\Delta E^{\circ\prime}$ values on the solvent, suggesting that a residual through-space electronic interaction is still operative; (ii) compounds **7−10** (having large π-delocalised spacer) show negligible dependence of $\Delta E^{\circ\prime}$ values on the solvent indicating that the through-bond electronic coupling is dominant.

Complexes **7** and **9** (as well as **15** and **17**) are two substitutional isomers, *para* and *meta* respectively. Their $\Delta E^{\circ\prime}$ experimental values are very similar. In contrast, in a purely through-bond model, the *para* isomer is expected to show stronger electronic interaction than the *meta* isomer, due to a higher degree of mixing between aryl and acetylenic orbitals.

A closer inspection of the available solid-state structures indicates that the "Co−Co" centres (a *naive* attempt of localisation of the redox cores) are not so far apart; i.e. the distance is about 4.43 Å in $[Co_2(CO)_6]_2(PhC{\equiv}C-C{\equiv}CPh)$[46] and 4.36 Å in $[Co_2(CO)_4(dppm)]_2(PhC{\equiv}C-C{\equiv}CPh)$[32], so that the substitution of CO groups by dppm does not alter substantially the aforementioned distance. Only in $[Co_2(CO)_6]_2(HC{\equiv}C-C_6H_4-C{\equiv}CH)$[47] such a distance increases up to 8.60 Å and in $[Co_2(CO)_6]_2(Me_3SiC{\equiv}C-C_6H_4-C_6H_4-C{\equiv}CSiMe_3)$[47] is 12.8 Å.

For complexes **12−19** we obtained slightly different values for $\Delta E^{\circ\prime}_{red}$ (measured at −30°C, when complete chemical reversibility is achieved for both reductions) and $\Delta E^{\circ\prime}_{ox}$ (measured at the same temperature for comparison purpose) (Table 2), although the trend is clearly the same. If the electronic communication were purely through-space one should foresee identical $\Delta E^{\circ\prime}$ values for oxidation and reduction. On the contrary, for extensive π-delocalization the $\Delta E^{\circ\prime}$ values depend on the character of both HOMO (depopulated by oxidation) and LUMO (populated by reduction) and should be, in principle, different. These orbitals have been postulated to be essentially Co−Co in character (bonding and antibonding, respectively) by simple EHT calculations on the model derivative $Co_2(CO)_6(H-C{\equiv}C-C{\equiv}C-H)$[48]. EHT calculations (CACAO package)[49] on the model complex $Co_2(CO)_4(H_2P-CH_2-PH_2)(H-C{\equiv}C-C{\equiv}C-H)$[**] confirm that the HOMO's composition is mainly metal−metal bonding in character (ca. 57%) with small contributions of

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[*] In the electrochemical context, $\Delta E^{\circ\prime}$ seems to be a good parameter to compare electronic interactions between redox centres in different solvents because it should be free of liquid junction potential errors, which effect each $E^{\circ\prime}$ equally.

[**] The geometry of the model complex $Co_2(CO)_4(H_2P-CH_2-PH_2)(H-C{\equiv}C-C{\equiv}C-H)$ was build up from the known structure of $Co_2(CO)_4(Ph_2P-CH_2-PPh_2)(Ph-C{\equiv}C-C{\equiv}C-Ph)$[32] by formal removal of the phenyl groups and substitution with hydrogen atoms (imposing a C−H distance of 1.10 Å and a P−H distance of 1.34 Å).

Table 2: Electrochemical data for complexes **12−19**, evaluated in THF containing $[Bu_4N][PF_6]$ (0.1 M), GC working electrode

Complex	$E°(0,0/0,1-)$[b]	$E°(0,1-/1-,1-)$[b]	$\Delta E°'_{red}$[b]	$E°(0,0/0,1+)$[b]	$E°(0,1+/1+,1+)$[b]	$\Delta E°'_{ox}$[b]	$\Delta E°'_{ox}$[c]
12	−1.67	−2.07	400	+0.61	+0.95	340	390
13	−1.66	−1.93	270	+0.57	+0.85	280	250
14	−1.56	−2.02	460	+0.61	+0.92	310	260
15	−1.62	−1.70	80	+0.66	+0.77	110	110
16	−1.57	−1.64	70	+0.74	+0.89	150	150
17	−1.66	−1.74	80	+0.68	+0.78	100	100
18	−1.60	−1.67	70	+0.73	+0.81	80	90
19	[a]	[a]	[a]	+0.75	+0.84	90	100

[a] Not evaluated because of overlapping of the reduction of the 9,10-bis(phenylethynyl)anthracene. − [b] At −30°C. − [c] At 20°C.

the butadiyne π-orbitals (ca. 5%) and of diphosphane (ca. 4%). Similarly, the LUMO's composition is mainly metal−metal antibonding in character (ca. 49%) with partial contribution of the diyne (ca. 11%) and negligible contribution of diphosphane. This similar but not identical composition does not allow any firm conclusion on the nature of interactions.

The bulk of results suggests that for all the compounds under investigation through-space interaction is always operative with different weight depending on the nature of the spacer L. The $\Delta E°'$ values (80−90 mV) evaluated for complexes **10** and **18**, having the larger aromatic spacer employed for the series, represent the limit of "purely" through-bond interactions.

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Experimental Section

Electrochemical Methods and Instrumentation: Electrochemical measurements were performed using EG&G PAR 273 or EG&G PAR 263 electrochemical analysers interfaced to personal computers employing PAR M270 Electrochemical Software. A standard three-electrode cell was constructed so that it allowed the tip of the reference system to approach the working electrode closely. An aqueous saturated calomel electrode (SCE) (separated from the cell solution with a Luggin probe) was the operational reference electrode at room temperature and all potentials are referred to SCE. A silver wire was used as a pseudo-reference for the low temperature measurements. The stability of the pseudo-reference electrode was verified by adding decamethylferrocene as an internal standard; the $Fc^*(0/1+)$ potential was evaluated in the same experimental conditions to be +0.11 V vs. SCE in THF[50][51]. The working electrode was a glassy carbon (GC) disk (diameter = 0.1 cm) sealed in inert resin. The voltammetric responses were recorded in THF $1\cdot10^{-3}$ M in electroactive material and 0.1 M in supporting electrolyte, $[Bu_4N][PF_6]$.

Preparation of $[Co_2(CO)_6]_2$-Diyne Complexes **1−11**: In a typical preparation stoichiometric amounts of the appropriate alkyne and $Co_2(CO)_8$ were allowed to react at room temperature, for 1 h in CH_2Cl_2 (35 ml/mmol) in a Schlenk tube under nitrogen. The reaction mixture was filtered through silica gel to remove any insoluble impurities and the filtrate taken to dryness in vacuum. The complex was then purified by recrystallisation from hexane at −20°C. Yields 70−80%. Since the spectroscopic characteristics of similar complexes have been previously discussed[52], the IR, ^{1}H- and ^{31}P-NMR spectroscopic data and elemental analyses of each new compound are simply reported as follows:

1: $C_{18}H_6Co_4O_{12}$: calcd. C 33.26, H 0.93; found C 33.20, H 0.90. − IR (CH_2Cl_2); ν_{CO}: 2091m, 2056vs, 2026vs cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 6.09 (s, 2 H, $\equiv CH$), 3.16 (s, 4 H, $-CH_2-$).

2: $C_{18}H_6Co_4O_{12}$: calcd. C 33.26, H 0.93; found C 33.00, H 0.92. − IR (CH_2Cl_2); ν_{CO}: 2100m, 2080s, 2057vs, 2029s, 2021s cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.74 (s, 6 H, $-CH_3$).

4: $C_{18}H_6Co_4O_{14}$: calcd. C 31.70, H 0.89; found C 31.50, H 0.90. − IR (CH_2Cl_2); ν_{CO}: 2103m, 2083s, 2061vs, 2034sh, 2028s cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 6.09 (d, 4 H, $^3J_{HH}$ = 5.6 Hz, $-CH_2-$), 2.87 (t, 2 H, $^3J_{HH}$ = 5.6 Hz, $-OH$),

5: $C_{30}H_{14}Co_4O_{14}$: calcd. C 43.20, H 1.69; found: C 43.15, H 1.72. − IR (CH_2Cl_2); ν_{CO}: 2105m, 2085s, 2063vs, 2034s, 2029s cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.36−6.99 (m, 10 H, Ph), 5.24 (s, 4 H, $-CH_2-$).

6: $C_{22}H_{18}Co_4O_{12}Si_2$: calcd. C 34.48, H 2.37; found C 34.40, H 2.30. − IR (CH_2Cl_2); ν_{CO}: 2099m, 2078s, 2059vs, 2032s, 2020s cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.42 (s, 18 H, $-CH_3$).

9: $C_{22}H_6Co_4O_{12}$: C 37.86, H 0.87; found: C 37.70, H 0.85. − IR (CH_2Cl_2); ν_{CO}: 2092m, 2060vs, 2028vs cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.70−7.30 (m, 4 H, C_6H_4), 6.39 (s, 2 H, $\equiv CH$).

10: $C_{28}H_{10}Co_4O_{12}$: calcd. C 43.44, H 1.30; found C 43.39, H 1.32. − IR (CH_2Cl_2); ν_{CO}: 2093m, 2057vs, 2028vs cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.60 (s, 8 H, Ph), 6.43 (s, 2 H, $\equiv CH$).

Preparation of $[Co_2(CO)_4(dppm)]_2$-Diyne Complexes **12−19**: Stoichiometric amounts of the appropriate alkyne and $Co_2(CO)_6(dppm)$, prepared according to a literature procedure[35], were heated at reflux in benzene for 2 h, under nitrogen. The hot reaction mixture was filtered through silica gel to remove any insoluble impurities and the filtrate taken to dryness in vacuum. The complex was then purified by recrystallisation from hexane/CH_2Cl_2 at −20°C. Yields 60−70%. Noteworthy, the co-ordination of two dppm ligands to the available Co−Co units is inferred by the presence of two complex multiplets in the region δ = 4.3−3.2, as expected for an ABX_2 pattern (X = ^{31}P) in the ^{1}H-NMR spectra[53] and by a single resonance in the region δ = 36−43 in the ^{31}P-NMR spectra.

13: $C_{64}H_{50}Co_4O_{10}P_4$: calcd. C 57.42, H 3.76; found C 57.382, H 3.7. − IR (CH_2Cl_2); ν_{CO}: 2033 (w), 2002vs, 1968m cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 7.56−7.04 (m, 40 H, Ph), 5.31 (s, br., 4 H, $-CH_2-$), 4.17, 3.22 (m, 4 H, $P-CH_2-P$), 2.20 (s, br., 2 H, $-OH$). − ^{31}P NMR ($CDCl_3$): δ = 39.8 (s).

14: $C_{76}H_{58}Co_4O_{10}P_4$: calcd. C 61.23, H 3.92; found C 61.19, H 3.89. − IR (CH_2Cl_2); ν_{CO}: 2034 (w), 2005vs, 1971m cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.50−6.40 (m, 50 H, Ph), 5.63 (s, 4 H, $-CH_2-$), 4.30, 3.26 (m, 4 H, $P-CH_2-P$). − ^{31}P NMR ($CDCl_3$): δ = 39.5 (s).

15: $C_{68}H_{50}Co_4O_8P_4$: calcd. C 60.29, H 3.72; found: C 60.25, H 3.70. − IR (CH_2Cl_2); ν_{CO}: 2021s, 1995vs, 1970s cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.78−6.92 (m, 44 H, Ph and C_6H_4), 5.82 (t, $^3J_{HP}$ = 3.1 Hz, 2 H, $\equiv CH$), 4.31, 3.20 (m, 4 H, $P-CH_2-P$). − ^{31}P NMR ($CDCl_3$): δ = 43.2 (s).

16: $C_{80}H_{58}Co_4O_8P_4$: calcd. C 63.76, H 3.88; found C 63.70, H 3.80. − IR (CH_2Cl_2); ν_{CO}: 2021s, 1997vs, 1971s cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.80−6.92 (m, 54 H, Ph and C_6H_4), 4.27, 3.25 (m, 4 H, $P-CH_2-P$). − ^{31}P NMR ($CDCl_3$): δ = 35.6 (s).

17: $C_{68}H_{50}Co_4O_8P_4$: calcd. C 60.29, H 3.72; found C 60.19, H 3.69. − IR (CH_2Cl_2); ν_{CO}: 2021s, 1997vs, 1969s cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.88−6.80 (m, 44 H, Ph and C_6H_4), 5.82 (t, $^3J_{HP}$ = 3.2 Hz, 2 H, $\equiv CH$), 3.62, 3.11 (m, 4 H, $P-CH_2-P$). − ^{31}P NMR ($CDCl_3$): δ = 43.1 (s).

18: $C_{74}H_{54}Co_4O_8P_4$: calcd. C 62.12, H 3.80; found C 62.00, H 3.60. − IR (CH_2Cl_2); ν_{CO}: 2021s, 1995vs, 1970s cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.00−6.80 (m, 48 H, Ph and C_6H_4), 5.81 (t, $^3J_{HP}$ = 3.1 Hz, 2 H, $\equiv CH$), 3.61, 3.18 (m, 4 H, $P-CH_2-P$). − ^{31}P NMR ($CDCl_3$): δ = 43.2 (s).

19: $C_{88}H_{62}Co_4O_8P_4$: calcd. C 65.77, H 3.89; found C 65.69, H 3.80. − IR (CH_2Cl_2); ν_{CO}: 2022s, 1997vs, 1973s cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.88−6.82 (m, 58 H, Ph and $C_{14}H_8$), 3.45, 3.23 (m, 4 H, $P-CH_2-P$). − ^{31}P NMR ($CDCl_3$): δ = 36.5 (s).

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