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The synthesis and reaction of *N*-phenyl alkynyl imine-hexacarbonyldicobalt complexes

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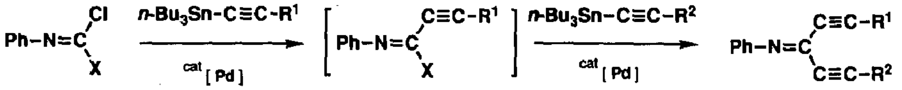
Abstract

N-Phenyl dialkynyl imines react with octacarbonyldicobalt to give *N*-phenyl dialkynyl imine-mono(hexacarbonyldicobalt) complexes. The structure of one of them, $[PhN{=}C(C{\equiv}CPh)_2]Co_2(CO)_6$ (**4b**), has been determined by X-ray crystallography, which shows that the phenyl ring on the imino nitrogen is oriented over the free acetylenic bond. The *N*-phenyl dialkynyl imine-mono(hexacarbonyldicobalt) complex thus formed undergoes cotrimerization with disubstituted alkynes to give pentasubstituted aryl alkynyl *N*-phenyl imines. *N*-Phenyl alkenyl alkynyl imines, prepared by 1,2-reduction of *N*-phenyl dialkynyl imines followed by isomerization, were also transformed into pentasubstituted aryl alkenyl *N*-phenyl imines via the corresponding *N*-phenyl alkynyl imine-hexacarbonyldicobalt complexes.

Introduction

The synthetic utility of the *N*-substituted isocyanide dichloride (**1a**) and chlorothioimidate (**1b**), which may be regarded as a synthetic equivalent to phosgene, has been limited because of their relatively low reactivity, i.e., useful synthetic reactions of **1** with carbon nucleophiles have scarcely been reported, though nucleophilic substitutions of **1a** with alcohols and amines give *N*-substituted iminocarbonates and urea derivatives respectively [1]. Recently, we reported palladium-catalyzed coupling reactions of **1** with alkynyltin compounds to give symmetrical and unsymmetrical *N*-phenyl dialkynyl imines (**2**) (eq. 1) [2].



(1)

1a X = Cl
1b X = SPh

2

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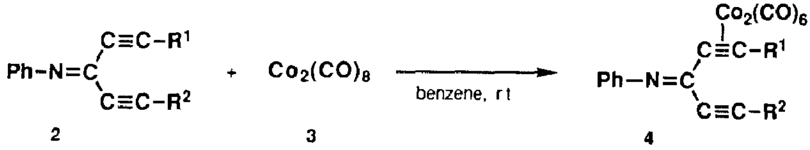
Furthermore, the reaction of the *N*-phenyl dialkynyl imine thus prepared with η^5-cyclopentadienyldicarbonylcobalt affords a mixture of η^4-cyclobutadiene cobalt complexes which can be derived from [2 + 2] dimers of **2** [3]. Here we describe the synthesis of *N*-phenyl alkynyl imine-hexacarbonyldicobalt complexes by the reaction of *N*-phenyl alkynyl imines with octacarbonyldicobalt and their cotrimerization with disubstituted alkynes to afford the corresponding pentasubstituted aryl *N*-phenyl imines.

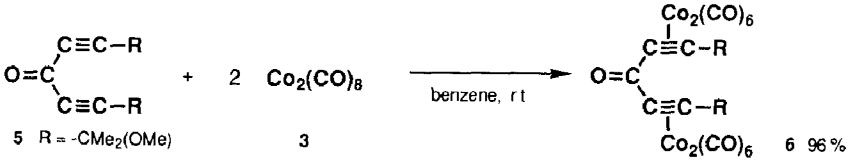
Results and discussion

Synthesis of N*-phenyl dialkynyl imine-hexacarbonyldicobalt complexes*

The reaction of *N*-phenyl dialkynyl imines (**2**) with ca. 1 equiv. of octacarbonyldicobalt (**3**) proceeded smoothly at room temperature in benzene and was complete in 30 min (eq. 2). Chromatographic purification on silica gel gave *N*-phenyl dialkynyl imine-hexacarbonyldicobalt complexes (**4**) as crystalline solids (Table 1, entries 1–3) or dark brown oils (entries 4, 5). Reaction with unsymmetrical hexynyl trimethylsilylethynyl *N*-phenyl imine, resulted in regioselective complexation of the hexacarbonyldicobalt moiety at the trimethylsilylethynyl group (entry 5). Noteworthy is that only one of the two acetylenic bonds of **2** reacted with **3** leaving the other acetylenic bond free even under more forcing conditions, such as in the presence of 2 equiv. of **3** at elevated temperature (110 °C). The molecular structure of **4b**, determined by X-ray crystallography, is shown in Fig. 1. The phenyl ring on the imino nitrogen is oriented over the free acetylenic bond to encumber the incoming **3**, which probably results in the selective formation of **4**. Indeed, dialkynyl ketone (**5**) readily reacted with 2 equiv. of **3** to give the dialkynyl ketone-bis(hexacarbonyldicobalt) complex (**6**) in high yield (eq. 3).



(2)



(3)

Table 1

Synthesis of *N*-phenyl dialkynyl imine-hexacarbonyldicobalt complexes

Entry	R^1	R^2	Product	Yield (%)
1	$SiMe_3$	$SiMe_3$	**4a**	92
2	Ph	Ph	**4b**	82
3	$CMe_2(OMe)$	$CMe_2(OMe)$	**4c**	95
4	n-Bu	n-Bu	**4d**	71
5	$SiMe_3$	n-Bu	**4e**	77

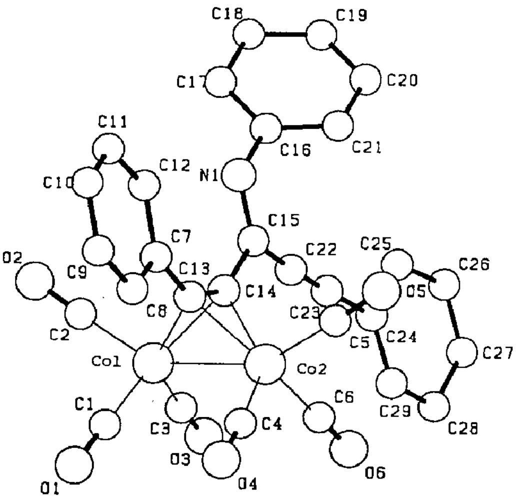


Fig. 1. Molecular structure of **4b**.

*Crystal structure of **4b***

Selected bond lengths and angles are listed in Table 2. The atomic coordinates and temperature factors are given in Table 3.

Table 2

Selected bond lengths (Å) and angles (°) with e.s.d. values in parentheses for **4b**

		C(22)–C(23)	1.185(8)
Co(1)–Co(2)	2.461(2)	C(13)–C(14)	1.349(7)
Co(1)–C(1)	1.816(7)	Co(2)–C(4)	1.809(7)
Co(1)–C(2)	1.776(7)	Co(2)–C(5)	1.773(6)
Co(1)–C(3)	1.829(7)	Co(2)–C(6)	1.820(7)
Co(1)–C(13)	1.977(5)	Co(2)–C(13)	1.966(5)
Co(1)–C(14)	1.963(5)	Co(2)–C(14)	1.961(5)
Co(2)–Co(1)–C(1)	99.6(2)	Co(1)–Co(2)–C(4)	98.4(2)
Co(2)–Co(1)–C(2)	148.1(2)	Co(1)–Co(2)–C(5)	150.7(2)
Co(2)–Co(1)–C(3)	98.0(2)	Co(1)–Co(2)–C(6)	99.5(2)
Co(2)–Co(1)–C(13)	51.2(1)	Co(1)–Co(2)–C(13)	51.6(1)
Co(2)–Co(1)–C(14)	51.1(2)	Co(1)–Co(2)–C(14)	51.2(2)
C(1)–Co(1)–C(2)	98.0(3)	C(4)–Co(2)–C(5)	100.2(3)
C(1)–Co(1)–C(3)	105.4(3)	C(4)–Co(2)–C(6)	103.3(3)
C(1)–Co(1)–C(13)	104.9(3)	C(4)–Co(2)–C(13)	101.9(3)
C(1)–Co(1)–C(14)	142.4(3)	C(4)–Co(2)–C(14)	139.8(3)
C(2)–Co(1)–C(3)	102.7(3)	C(5)–Co(2)–C(6)	98.0(3)
C(2)–Co(1)–C(13)	98.5(3)	C(5)–Co(2)–C(13)	102.2(2)
C(2)–Co(1)–C(14)	100.4(3)	C(5)–Co(2)–C(14)	101.1(2)
C(3)–Co(1)–C(13)	139.9(3)	C(6)–Co(2)–C(13)	144.1(3)
C(3)–Co(1)–C(14)	102.2(3)	C(6)–Co(2)–C(14)	107.0(3)
C(13)–Co(1)–C(14)	40.0(2)	C(13)–Co(2)–C(14)	40.2(2)
Co(1)–C(13)–Co(2)	77.2(2)	Co(1)–C(14)–Co(2)	77.7(2)
Co(1)–C(13)–C(7)	133.0(4)	Co(1)–C(14)–C(15)	131.5(4)
Co(2)–C(13)–C(7)	135.9(4)	Co(2)–C(14)–C(15)	134.3(4)
Co(1)–C(13)–C(14)	69.4(3)	Co(1)–C(14)–C(13)	70.5(3)
Co(2)–C(13)–C(14)	69.7(3)	Co(2)–C(14)–C(13)	70.1(3)
C(7)–C(13)–C(14)	142.9(5)	C(13)–C(14)–C(15)	144.7(5)

Table 3

Atomic co-ordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10$) with e.s.d.'s in parentheses for **4b**

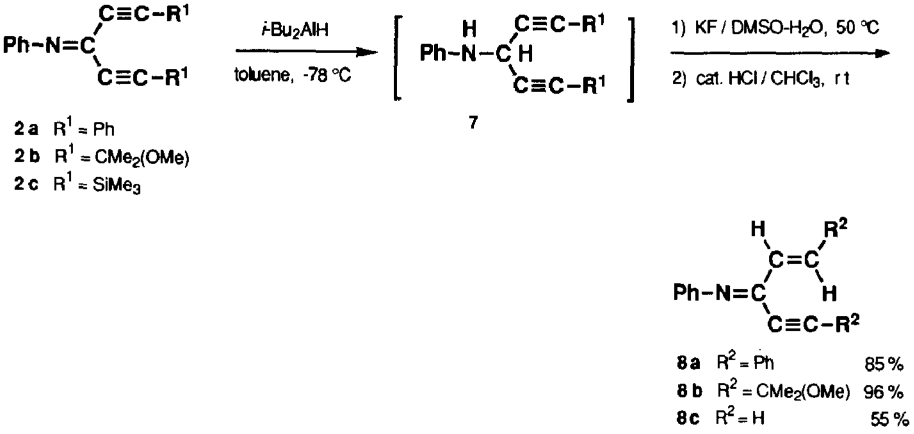
	x	y	z	B_{eq} ^{a}
Co(1)	8088.8(6)	7467.4(4)	8880.8(8)	40.8(2)
Co(2)	7605.2(6)	7939.7(3)	6712.7(7)	37.6(2)
O(1)	7593(6)	8490(2)	10703(5)	94(3)
O(2)	9793(5)	6863(2)	10507(6)	84(2)
O(3)	6155(4)	6653(3)	9018(5)	81(2)
O(4)	7062(5)	9148(2)	7763(6)	97(3)
O(5)	8124(4)	8213(2)	3894(5)	68(2)
O(6)	5418(3)	7369(2)	6276(6)	78(2)
N(1)	9947(4)	6579(2)	6150(5)	42(2)
C(1)	7774(6)	8091(3)	10009(6)	61(3)
C(2)	9109(6)	7105(3)	9893(6)	57(2)
C(3)	6900(5)	6955(3)	9009(6)	57(2)
C(4)	7249(5)	8684(3)	7333(7)	58(2)
C(5)	7927(5)	8114(2)	5012(6)	46(2)
C(6)	6256(5)	7589(3)	6428(6)	52(2)
C(7)	10121(4)	8165(2)	7585(5)	36(2)
C(8)	10117(5)	8770(3)	7989(6)	44(2)
C(9)	11099(5)	9096(3)	8079(6)	48(2)
C(10)	12092(5)	8815(3)	7812(6)	52(2)
C(11)	12126(5)	8215(3)	7406(6)	53(2)
C(12)	11142(5)	7882(3)	7303(6)	45(2)
C(13)	9088(4)	7816(2)	7502(5)	38(2)
C(14)	8664(4)	7285(2)	7074(5)	37(2)
C(15)	8923(4)	6713(2)	6416(5)	37(2)
C(16)	10186(4)	6025(2)	5492(6)	42(2)
C(17)	11021(5)	5662(3)	6031(7)	53(2)
C(18)	11255(6)	5101(3)	5382(8)	69(3)
C(19)	10702(7)	4938(3)	4217(9)	74(3)
C(20)	9931(6)	5308(3)	3662(8)	66(3)
C(21)	9682(5)	5859(3)	4292(7)	54(2)
C(22)	7987(4)	6314(2)	6174(6)	39(2)
C(23)	7240(5)	5984(2)	5916(6)	44(2)
C(24)	6364(5)	5575(3)	5505(6)	47(2)
C(25)	6643(6)	5029(3)	4871(7)	58(2)
C(26)	5782(8)	4654(3)	4426(8)	76(3)
C(27)	4699(7)	4816(4)	4647(9)	87(4)
C(28)	4430(6)	5346(4)	5270(9)	78(3)
C(29)	5259(5)	5729(3)	5703(7)	57(3)

^{a} $B_{eq} = (4/3)\Sigma_i \Sigma_j \beta_{ij} a_i a_j$

The configuration about each cobalt atom is best described as a trigonal bipyramid, with one axial (C2, C5) and two equatorial (C1, C3, C4, C6) carbonyl ligands. The midpoint of the C≡C bond occupies a coordination site in the equatorial plane. The axial and equatorial carbonyl ligands are differentiated in terms of their Co–C distances; the average bond distances between cobalt and carbonyl carbon atoms are 1.775(5) Å for the axial carbonyl, and 1.819(4) Å for the equatorial carbonyls. A similar difference in bond distances between cobalt and carbonyl carbon atoms has been found in a low-temperature neutron diffraction study of the tricobalt carbon cluster [4].

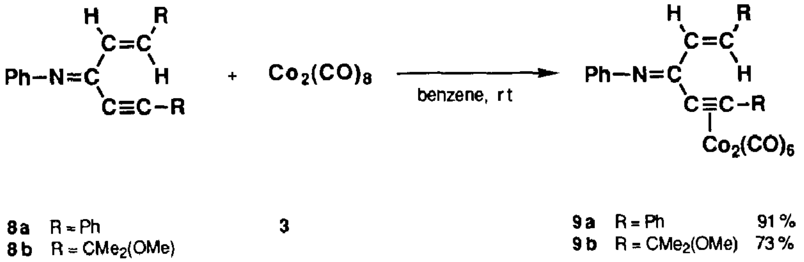
Preparation of N*-phenyl alkenyl alkynyl imines and synthesis of their hexacarbonyldicobalt complexes*

1,2-Reduction took place on treatment of **2** with diisobutylaluminium hydride to give **7**, which was then isomerized to *N*-phenyl alkenyl alkynyl imines (**8**) by potassium fluoride [5]. Though a direct introduction of alkenyl group onto imino carbon by palladium-catalyzed coupling reaction of **1** with alkenyltin compounds was unsuccessful [2], the reduction-isomerization procedure provides a facile route to *N*-phenyl alkenyl alkynyl imines (eq. 4).



(4)

N-Phenyl alkenyl alkynyl imines (**8**) thus obtained also reacted with **3** to give the corresponding cobalt complexes (**9**) in good yields (eq. 5).



(5)

Reaction of N*-phenyl alkynyl imine-hexacarbonyldicobalt complexes (4 and 9) with alkynes*

Attempted reactions of the cobalt complexes (**4** and **9**) with olefins (intermolecular Pauson–Khand reaction) have been unsuccessful and gave only tarry products. On the other hand, both **4** and **9** underwent cotrimerization with an excess of disubstituted alkynes to afford aromatized products, pentasubstituted aryl *N*-phenyl imines (**10**) (eq. 6, Table 4) [6]. However, the reaction with phenylacetylene yielded the self-trimerization product of phenylacetylene, viz., triphenylbenzene, suggesting

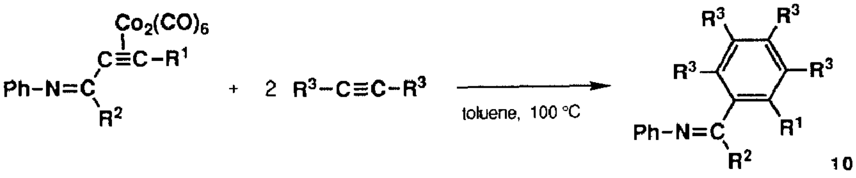
Table 4

Reaction of **6** and **9** with disubstituted alkynes

Entry	R^1	R^2	R^3	Product	Yield (%)
1	$SiMe_3$	$C\equiv CSiMe_3$	Ph	**10a**	60
2	$SiMe_3$	$C\equiv CSiMe_3$	n-Bu	**10b**	50
3	$SiMe_3$	$C\equiv CSiMe_3$	[a]	**10c**	48 [b]
4	Ph	$C\equiv CPh$	n-Bu	**10d**	46
5	$CMe_2(OMe)$	$C\equiv CCMe_2(OMe)$	Ph	**10e**	86
6	$SiMe_3$	$C\equiv C(n\text{-}Bu)$	Ph	**10f**	41
7	Ph	$CH{=}CHPh$	n-Bu	**10g**	61
8	$CMe_2(OMe)$	$CH{=}CHCMe_2(OMe)$	Ph	**10h**	85

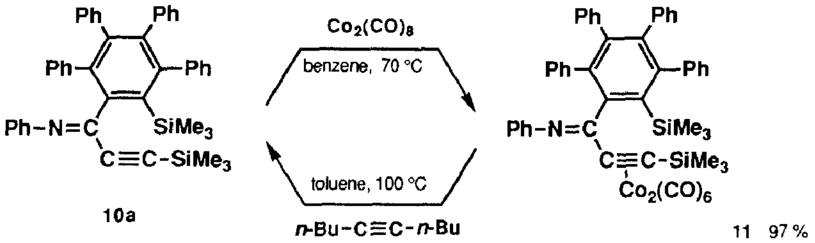
[a] n-BuC≡CPh was used. [b] A mixture of regioisomers.

that an exchange of alkynyl ligand on the cobalt complex with phenylacetylene proceeds faster than the cotrimerization.



(6)

Further reaction of **10a** with **3** gave *N*-phenyl aryl alkynyl imine-hexacarbonyldicobalt complex (**11**) in high yield (97%). However, reaction of **11** with 5-decyne resulted in exchange of alkynyl ligands to regenerate **10a** (eq. 7).



(7)

Thus our reaction opens the way to the synthesis of highly substituted aryl *N*-phenyl imines (**10**), which are difficult to obtain by conventional methods.

Experimental

Materials and methods

Infrared spectra were recorded with a Hitachi 270-30 spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Varian VXR-200 spectrometer. Mass spectra were recorded with a JEOL JMS-D300 spectrometer. Melting points were measured with a Yamato-MP apparatus and are uncorrected.

All reactions were performed under nitrogen by use of Schlenk tube techniques. Symmetrical and unsymmetrical dialkynyl *N*-phenyl imines (**2**) and dialkynyl ketones (**5**) were prepared by published procedures [2]. Octacarbonyldicobalt was purchased from Strem Chemicals, Inc. and used without further purification. Benzene and toluene were freshly distilled under nitrogen from lithium aluminium hydride before use.

General procedure of synthesis of N*-phenyl alkynyl imine-hexacarbonyldicobalt complexes (4 and 9)*

A solution of octacarbonyldicobalt (3, 1.0 mmol) and an *N*-phenyl alkynyl imine (0.9 mmol) in benzene (3 ml) was stirred at ambient temperature for 30 min. After evaporation of the solvent, silica gel column chromatography of the residue (hexane–ether as eluent) provided the *N*-phenyl alkynyl imine-hexacarbonyldicobalt complexes.

Physical and spectral data were as follows:

4a: yield 92%; m.p. 32–33 °C (CH_3OH); ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9 H), 0.38 (s, 9 H), 7.10–7.40 (m, 5 H); ^{13}C NMR {^{1}H} ($CDCl_3$): δ −1.00, 0.41, 81.29, 98.78, 102.86, 105.15, 121.27, 125.40, 128.27, 148.56, 150.55, 199.00–200.00 (br s); IR (KBr): 2096, 2060, 2032, 1580, 1555, 1254, 842 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 555 (*M* − CO, 10%), 527 (*M* − 2CO, 50%), 499 (*M* − 3CO, 60%), 471 (*M* − 4CO, 25%), 443 (*M* − 5CO, 60%), 415 (*M* − 6CO, 100%); Anal. Found: H, 3.75; C, 46.87; N, 2.44. $C_{23}H_{23}NO_6Si_2Co_2$ calcd.: H, 3.97; C, 47.34; N, 2.40%.

4b: yield 82%; m.p. > 123 °C (dec., hexane–CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 7.00–8.00 (m, 15 H); IR (KBr): 2204, 2096, 2064, 2028, 1624, 1590, 1528 cm^{-1}; mass spectrum (FD): *m/e* (relative intensity) 591 (*M*, 100%); Anal. Found: H, 2.39; C, 58.86; N, 2.46. $C_{29}H_{15}NO_6Co_2$ calcd.: H, 2.56; C, 58.91; N. 2.37%.

4c: yield 95%; m.p. 37–38 °C (hexane); ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 6 H), 1.66 (s, 6 H), 2.98 (s, 3 H), 3.37 (s, 3 H), 6.95–7.40 (m, 5 H); IR (KBr): 2100, 2064, 2032, 1590, 1558 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 555 (*M* − CO, 9%), 527 (*M* − 2CO, 42%), 499 (*M* − 3CO, 97%), 471 (*M* − 4CO, 2%), 443 (*M* − 5CO, 42%) 415 (*M* − 6CO, 100%); Anal. Found: H, 4.05; C, 51.34; N, 2.45. $C_{25}H_{23}NO_8Co_2$ calcd.: H, 3.97; C, 51.48; N, 2.40%.

4d: yield 71%; oil; ^{1}H NMR ($CDCl_3$): δ 0.83 (t, *J* 6.6 Hz, 3 H), 0.98 (t, *J* 7.0 Hz, 3 H), 1.10–1.80 (m, 8 H), 2.25 (t, *J* 6.8 Hz, 2 H), 2.96 (t, *J* 7.4 Hz, 2 H), 7.00–7.42 (m, 5 H); IR (neat): 2220, 2096, 2060, 2028, 1590, 1566 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 523 (*M* − CO, 3%), 495 (*M* − 2CO, 37%), 467 (*M* − 3CO, 41%), 439 (*M* − 4CO, 26%), 411 (*M* − 5CO, 56%), 383 (*M* − 6CO, 100%).

4e: yield 77% (a mixture of syn and anti isomers); oil; ^{1}H NMR ($CDCl_3$): δ 0.10 and 0.36 (s, 9 H), 0.83 and 0.99 (t, *J* 8.0 and 7.0 Hz, 3 H), 1.15–1.82 (m, 4 H), 2.25 and 2.97 (t, *J* 8.0 and 8.4 Hz, 2 H), 7.08–7.39 (m, 5 H); IR (neat): 2096, 2060, 2036, 1582 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 539 (*M* − CO, 9%), 511 (*M* − 2CO, 49%), 483 (*M* − 3CO, 63%), 455 (*M* − 4CO, 23%), 427 (*M* − 5CO, 66%), 399 (*M* − 6CO, 100%).

9a: yield 91%; m.p. > 110 °C (dec., hexane–CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 6.85–7.70 (m, 17 H); IR (KBr): 2096, 2064, 2050, 2025, 1616, 1590, 1580, 1560 cm^{-1}; Anal. Found: H, 2.80; C, 58.66; N, 2.24. $C_{29}H_{17}NO_6Co_2$ calcd.: H, 2.89; C, 58.71; N, 2.36%.

9b: yield 73%; oil; ^{1}H NMR ($CDCl_3$): δ 1.16 (s, 6 H), 1.62 (s, 6 H), 2.98 (s, 3 H), 3.36 (s, 3 H), 6.18 (d, *J* 16.6 Hz, 1 H), 6.43 (d, *J* 16.6 Hz, 1 H), 6.69–6.79 (m, 2 H), 6.95–7.10 (m, 1 H), 7.26–7.37 (m, 2 H); IR (neat): 2096, 2028, 1590 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 557 (*M* – CO, 9%), 529 (*M* – 2CO, 40%), 501 (*M* – 3CO, 90%), 445 (*M* – 5CO, 41%), 417 (*M* – 6CO, 100%).

*Synthesis of dialkynyl ketone-bis(hexacarbonyldicobalt) complex (**6**)*

A solution of **3** (0.21 mmol) and dialkynyl ketone (**5**, 0.10 mmol) in benzene (1.0 ml) was stirred at ambient temperature for 1 h. After evaporation of the solvent, silica gel column chromatography of the residue (hexane: ether = 20 : 1) provide the dialkynyl ketone-bis(hexacarbonyldicobalt) complex (**6**) as dark brown solid: yield 96%, m.p. 63–65 ° C (hexane–ether); ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 12 H), 3.30 (s, 6 H); IR (KBr): 2104, 2052, 1584 cm^{-1}; Anal. Found: H, 2.13; C, 37.55. $C_{25}H_{18}O_{15}Co_4$ calcd.: H, 2.28; C, 37.81%.

General procedure of synthesis of N*-phenyl alkenyl alkynyl imines (**8**)*

To a stirred solution of **2** (4.0 mmol) in toluene (8.0 ml) was added a hexane solution of diisobutylaluminium hydride (1.0 *M*, 4.5 mmol) at –78 ° C. The reaction mixture was maintained at that temperature for 2 h and then warmed gradually to room temperature. After quenching with saturated aqueous solution of $NaHCO_3$, usual extractive work-up gave a mixture of **7** and **8**, then the mixture was treated with sat. aq. KF–DMSO–THF (1 : 1 : 1, 12 ml) at 60 ° C for 4 h. Extractive work-up followed by treatment with dil. HCl afforded **8**.

Physical and spectral data were as follows:

8a: yield 85%; oil; ^{1}H NMR ($CDCl_3$): δ 6.55–6.70 (m, 2 H), 7.06–7.69 (m, 15 H); ^{13}C NMR {^{1}H} ($CDCl_3$): δ 81.90, 97.19, 121.17, 125.09, 127.73, 128.01, 128.39, 128.46, 128.90, 129.47, 129.77, 129.93, 132.30, 135.58, 141.16, 150.72, 151.24; IR (neat): 2224, 2196, 1632, 1592, 1552, 1492, 1450, 1324, 1188, 968 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 307 (*M*, 98%), 306 (*M* – H, 100%); Anal. Found: H, 5.50; C, 89.79; N, 4.45. $C_{23}H_{17}N$ calcd.: H, 5.57, C, 89.87; N, 4.56%.

8b: yield 96%; oil; ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 6 H), 1.38 (s, 6 H), 3.08 (s, 3 H), 3.23 (s, 3 H), 6.50 (d, *J* 16.2 Hz, 1 H), 6.67 (d, *J* 16.2 Hz, 1 H), 6.95–7.36 (m, 5 H); IR (neat): 2220, 1594, 1580, 1575, 1174, 1076 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 300 (*M* + H, 100%), 284 (*M* – Me, 20%), 268 (*M* – OMe, 95%); Anal. Found: H, 8.42; C, 76.30; N, 4.51. $C_{19}H_{25}NO_2$ calcd.: H, 8.42; C, 76.22; N, 4.68%.

8c: yield 55%; b.p. 120–125 °C/2 mmHg (Kugelrohr); ^{1}H NMR ($CDCl_3$): δ 3.22 (s, 1 H), 5.91 (d, *J* 9.6 Hz, 1 H), 6.27 (d, *J* 17.2 Hz, 1 H), 6.74 (dd, *J* 9.6, 17.2 Hz, 1 H), 7.00–7.41 (m, 5 H); ^{13}C NMR {^{1}H} ($CDCl_3$): δ 74.68, 85.30, 120.42, 125.28, 126.78, 128.54, 138.00, 150.02, 150.46; IR (neat): 3292, 2100, 1576 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 155 (*M*, 82%), 154 (*M* – H, 100%), 128 (*M* – CH=CH_2, 24%); Anal. Found: H, 5.68; C, 85.14; N, 8.91. $C_{11}H_9N$ calcd.: H, 5.85; C, 85.13; N, 9.02%.

General procedure of reaction of N*-phenyl alkynyl imine-hexacarbonyldicobalt complexes (**4** and **9**) with alkynes*

A solution of *N*-phenyl alkynyl imine-hexacarbonyldicobalt complex (**4** or **9**, 0.1 mmol) and an alkyne (0.5 mmol) in toluene (0.6 ml) was stirred at 100 ° C for 3 h.

After evaporation of the solvent, preparative TLC on silica gel afforded pentasubstituted aryl *N*-phenyl imine (**10**).

Physical and spectral data were as follows:

10a: yield 60%; colorless oil; ^{1}H NMR ($CDCl_3$): δ – 0.04 (s, 9 H), 0.03 (s, 9 H), 6.71–7.33 (m, 25 H); ^{13}C NMR {^{1}H} ($CDCl_3$): δ –0.99 (Si*Me*$_3$), 3.48 (Si*Me*$_3$), 154.95 (*C*=N); IR (neat): 1580, 1252, 1136, 910, 844, 732, 698 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 653 (*M*, 12%), 638 (*M* – Me, 100%).

10b: yield 50%; colorless solid, m.p. 112–114° C (hexane–CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 9 H), 0.37 (s, 9 H), 0.88–1.05 (m, 12 H), 1.25–1.70 (m, 16 H), 2.55–2.82 (m, 8 H), 7.15–7.43 (m, 5 H); IR (KBr): 2936, 1582, 1466, 1252, 860, 844 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 573 (M, 61%), 572 (*M* – H, 100%), 558 (*M* – Me, 28%), 500 (*M* – Me_3Si, 20%); Anal. Found: H, 10.65; C, 77.21; N, 2.41. $C_{37}H_{59}NSi_2$ calcd.: H, 10.36; C, 77.42; N, 2.44%.

10c: yield 48% (a mixture of regioisomers); colorless oil; ^{1}H NMR ($CDCl_3$): δ 0.01, 0.11, 0.41, 0.45 (s × 4, 18 H), 0.50–2.72 (m, 18 H), 6.67–7.42 (m, 15 H); IR (neat): 1582, 1252, 846 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 613 (*M*, 63%), 612 (*M* – H, 63%), 598 (*M* – Me, 100%).

10d: yield 46%; colorless oil; ^{1}H NMR ($CDCl_3$): δ 0.62–2.80 (m, 36 H), 6.52–6.60 (m, 2 H), 7.00–7.36 (m, 13 H); IR (neat): 2200, 1586, 1464 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 581 (*M*, 55%), 580 (*M* – H, 100%).

10e: yield 86%; colorless oil; ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 3 H), 1.71 (s, 3 H), 1.59 (s, 3 H), 1.72 (s, 3 H), 2.82 (s, 3 H), 3.22 (s, 3 H), 6.48–7.25 (m, 25 H); IR (neat): 2220, 1592, 1446, 1256, 1170, 1120, 1074, 698 cm^{-1}; mass spectrum (EI, 20 eV) *m/e* (relative intensity) 653 (*M*, 18%), 623 (*M* – OMe + H, 100%).

10f: yield 41%; colorless oil; ^{1}H NMR ($CDCl_3$): δ 0.02 (s, 9 H), 0.70–1.40 (m, 7 H), 2.04 (t, *J* 6.8 Hz, 2 H), 6.70–7.32 (m, 25 H); IR (neat): 2212, 1592, 1488, 1446, 910, 870, 840, 768, 734, 698 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 637 (*M*, 24%), 622 (*M* – Me, 100%).

10g: yield 61%; colorless oil; ^{1}H NMR ($CDCl_3$): δ 0.60–2.82 (m, 36 H), 6.30–6.38 (m, 2 H), 6.51 (d, *J* 16.0 Hz, 1 H), 6.67 (d, *J* 16.0 Hz, 1 H), 6.96–7.45 (m, 13 H); IR (neat): 1620, 1590, 1484 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 583 (*M*, 88%), 526 (*M* – Bu, 61%).

10h: yield 85%; colorless solid, m.p. 174–176° C (hexane–CH_2Cl_2); ^{1}H NMR (C_6D_6): δ 0.97 (s, 3 H), 1.03 (s, 3 H), 1.28 (s, 3 H), 2.03 (s, 3 H), 2.88 (s, 3 H), 3.05 (s, 3 H), 6.22 (d, *J* 16.2 Hz, 1 H), 6.42 (d, *J* 16.2 Hz, 1 H), 6.60–7.34 (m, 23 H), 7.75–7.82 (m, 2 H); ^{13}C NMR {^{1}H} ($CDCl_3$): δ 169.24 (*C*=N); IR (KBr): 1594, 1170, 1074 cm^{-1}; mass spectrum (EI, 20 eV): *m/e* (relative intensity) 655 (*M*, 8%), 624 (*M* – OMe, 13%) 582 (*M* – C(OMe)Me_2, 100%); Anal. Found: H, 6.85; C, 85.96; N, 2.06. $C_{47}H_{45}NO_2$ calcd.: H, 6.92; C, 86.07; N, 2.14%.

Reaction of N*-phenyl aryl alkynyl imine (**10a**) with **3***

A mixture of **10a** (0.08 mmol) and **3** (0.1 mmol) in benzene solution (0.5 ml) was stirred at 70° C for 2 h. After evaporation of the solvent, silica gel column chromatography of the residue (hexane : ether = 40 : 1) provided **11** as dark brown oil: yield 97%; ^{1}H NMR ($CDCl_3$): δ 0.13 (s, 9 H), 0.36 (s, 9 H), 6.08–7.70 (m, 25 H); IR (neat): 2092, 2056, 2020, 2010, 1574, 1532, 1252 cm^{-1}.

X-Ray diffraction study of ***4b***

Crystal data are as follows: $C_{29}H_{15}NO_6Co_2$, $f_W = 591.31$, orthorhombic, space group $P2_12_12_1$, a 12.021(3), b 22.112(9), c 9.919(3) Å, U 2637(1) Å^3, D_c 1.489 g cm^{-3}, $Z = 4$, $F(000) = 1192$, λ(Mo-K_α) 0.71069 Å, μ 13.53 cm^{-1}, T 25 °C, crystal size 0.6 × 0.3 × 0.1 mm. Unit cell parameters were refined with 2θ angles of 20 reflections ($10 \leq 2\theta \leq 20°$). A total of 2643 unique reflections in the region of $2\theta \leq 50°$ were collected on a Rigaku AFC-5 diffractometer by the ω–2θ scan technique; scan speed 6° min^{-1} for ω, scan width $\Delta\omega = 1.0 + 0.5 \tan\theta°$, and background counting time 4 s on each side. Three standard reflections monitored every 100 measurements showed no significant variation. A total of 2152 reflections with $F_o > 3\sigma(F_o)$ were used for structure determination. The structure was solved by the heavy-atom method and anisotropically refined by the block-diagonal least squares method. Absorption corrections were applied after isotropic least squares refinement by an empirical method based on the differences between the observed and calculated structure factors [7]. H atoms were located from a difference electron density map and refined with isotropic temperature factors set equal to B_{eq} values of the bonded atoms. Atomic scattering factors were evaluated by analytical procedures $[f = \Sigma[a_i \exp(-b_i\lambda^{-2}\sin^2\theta)] + c \quad (i = 1 \cdots 4)]$ and corrected for anomalous dispersion effects of Co with $f' = 0.299$ and $f'' = 0.973$ [8]. Weights were taken as $w = [\sigma^2(F_o) + 0.00079(F_o)^2]^{-1}$ for the reflections with $w^{1/2}|\Delta F| < 4$, and $w = 0$ otherwise. Final R, R_w and S (goodness of fit) were 0.038, 0.046 and 1.080 for 2151 reflections, respectively. Tables of anisotropic thermal parameters, structure factors, and bond lengths and angles are available from the authors.

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