Rearrangements of >C=N– Functionalities promoted by Cobalt(I): Reactivity of Cyclopentadienylbis(ethylene)cobalt(I) with Dibenzophenone Azine, Benzophenone Oxime, Benzylidene(phenyl)amine and Crystal Structure Determinations of the Products†

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The reaction of $[Co(cp)(C_2H_4)_2]$ (**1**) with various >C=N– organic functionalities was explored. The results are very different depending on the substituents at the imino group. Dibenzophenone azine, $Ph_2C=N-N=CPh_2$, oxidatively adds to (**1**) forming a diamagnetic binuclear cobalt(II) complex $[\{Co(cp)\}_2(\mu-Ph_2C=N)_2]$ (**2**) [Co–Co 2.335(1) Å]. The reaction of (**1**) with benzophenone oxime, $Ph_2C=NOH$, led, *via* a preliminary oxidative addition of the O–H bond to the metal, to the formation of a non-symmetric binuclear cobalt(II) complex $[\{Co(cp)\}_2(\mu-Ph_2C=N)(\mu-Ph_2C=NO)]$ (**3**) [Co–Co 2.426(1) Å]. Benzylidene(phenyl)amine, PhCH=NPh, undergoes a sort of *ortho*-metallation reaction with (**1**), the resulting metallacycle functioning as a ligand for a second [Co(cp)] unit. The binuclear complex $[\{Co(cp)\}_2(\mu-PhNCH_2C_6H_4)]$ [Co–Co 2.375(1) Å] (**4**) is formed. Compounds (**2**)—(**4**) were characterized by single-crystal *X*-ray analysis: (**2**), space group *Fdd*2, *a* = 18.346(3), *b* = 39.348(7), *c* = 8.359(2) Å, *Z* = 8, *R* = 0.046 for 1463 independent observed reflections; (**3**), space group $P2_1/c$, *a* = 10.009(1), *b* = 30.433(3), *c* = 10.344(1) Å, β = 108.93(1)°, *Z* = 4, *R* = 0.041 for 2 274 independent observed reflections; (**4**), space group $P2_1/n$, *a* = 9.674(1), *b* = 8.512(1), *c* = 22.741(3) Å, β = 95.90(1)°, *Z* = 4, *R* = 0.040 for 1 845 independent observed reflections.

The 16 valence-electron (v.e.) species [Co(cp)L] (cp = η^5-C_5H_5), thermally or photochemically generated from $[Co(cp)(CO)_2]$, shows its versatility in binding a variety of organic functionalities and assembling >C=C< and –C≡C– groups in some exotic molecules.[1,2] The highly unsaturated species [Co(cp)] is much more easily accessible from $[Co(cp)(C_2H_4)_2]$.[3] Its reactivity with organic functionalities, though not very much explored, is not limited to the simple binding of the organic ligand, as with [Co(cp)L],[1b] but the organic ligand becomes a sort of aggregating agent for a polymetallic assemble.[4–6] This leads to a sort of stepwise polymetallic activation and fixation of an organic functionality. Focusing on this general behaviour of $[Co(cp)(C_2H_4)_2]$,[3] we investigated its reactivity with very different organic groups containing a >C=N– double bond, such as a ketazine, a ketoxime, and a Schiff base. The [Co(cp)] 14 v.e. fragment is able to cleave N–N, O–H, and C–H bonds and reacts with the preformed mononuclear species to form binuclear diamagnetic cobalt(II) complexes containing a metal–metal bond.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The synthesis of $[Co(cp)(C_2H_4)_2]$, (**1**), was carried out as previously reported.[3] Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer and ^{1}H n.m.r. spectra with 200 AC and 60 VP Brucker instruments.

Reactions of Complex (**1**).—*With benzophenone azine*, $Ph_2C=N-N=CPh_2$: *synthesis of complex* (**2**). A toluene solution (50 cm^3) of complex (**1**) (1.21 g, 6.72 mmol) was treated with $Ph_2C=N-N=CPh_2$ (1.21 g, 3.36 mmol) at room temperature for 2 d. The solvent was partially evaporated, then n-hexane was added (50 cm^3). On cooling at −30 °C the solution gave crystals of complex (**2**) (*ca.* 65%) (Found: C, 70.80; H, 4.95; N, 4.40. Calc. for $C_{36}H_{30}Co_2N_2$: C, 71.05; H, 4.95; N, 4.60%). ν(C=N) (Nujol) 1 595 cm^{-1}. Proton n.m.r. (C_6D_6): δ 4.35 (s, cp) and 7.35 (m, Ph).

With benzophenone oxime, $Ph_2C=NOH$: *synthesis of complex* (**3**). Complex (**1**) (1.96 g, 10.9 mmol) was added as a solid to a toluene solution (75 cm^3) of $Ph_2C=NOH$ (2.15 g, 10.9 mmol). The solution became green, then maroon with significant evolution of ethylene. It was kept at room temperature overnight. A small amount of maroon solid was removed by filtration. The resulting solution was partially evaporated, then n-hexane (20 cm^3) was added. A brown crystalline solid (67%) was obtained on standing (Found: C, 71.05; H, 5.30; Co, 17.95; N, 4.60. Calc. for $C_{36}H_{30}Co_2N_2O\cdot0.33C_7H_8$: C, 70.20; H, 5.05; Co, 18.00; N, 4.30%). I.r. (Nujol): weak C=N bands at 1 600 cm^{-1}. Proton n.m.r. (C_6D_6): δ 4.37 (s, cp), 4.52 (s, cp), 6.80—7.40 (m, Ph), and 8.2—7.8 (m, Ph).

With benzylidene(phenyl)amine, PhCH=NPh: *synthesis of complex* (**4**). Complex (**1**) (1.20 g, 6.7 mmol) was added to a tetrahydrofuran (thf) solution (50 cm^3) of PhCH=NPh (1.11 g, 6.1 mmol). The resulting brown solution was kept at room temperature for 1 d until the thf was completely evaporated, then the solid residue was dissolved in n-hexane (10 cm^3). In a few days the solution gave a green crystalline solid (31%). The yield can be increased up to 60% by cooling the solution

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Experimental data for the *X*-ray diffraction studies on crystalline complexes (**2**)—(**4**)

Complex	(**2**)	(**3**)	(**4**)
Crystal habit and colour	Black-brown opaque prisms	Black-brown opaque prisms	Black-brown opaque prisms
Formula	$C_{36}H_{30}Co_2N_2$	$C_{36}H_{30}Co_2N_2O$	$C_{23}H_{21}Co_2N$
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Fdd*2	$P2_1/c$	$P2_1/n$
Cell parameters at 295 K[a]			
a/Å	18.346(3)	10.009(1)	9.674(1)
b/Å	39.348(7)	30.433(3)	8.512(1)
c/Å	8.359(2)	10.344(1)	22.741(3)
α/°	90	90	90
β/°	90	108.93(1)	95.90(1)
γ/°	90	90	90
U/Å^3	6 034(2)	2 980.4(5)	1 863(1)
Z	8	4	4
D_c/g cm^{-3}	1.340	1.392	1.531
F(000)	2 512	1 288	880
M	608.5	624.5	429.3
Crystal dimensions/mm	0.19 × 0.29 × 0.56	0.34 × 0.48 × 0.51	0.30 × 0.45 × 0.50
μ/cm^{-1}	11.23	11.41	17.83
Diffractometer	Philips PW 1100	Siemens AED	Philips PW 1100
Diffraction geometry	Equatorial	Equatorial	Equatorial
Scan type	ω—2θ	ω—2θ	ω
Scan speed	0.100° s^{-1}	3—12° min^{-1}	0.100° s^{-1}
Scan width/°	1.00	*b*	1.60
Radiation	*c*	*d*	*c*
2θ Range/°	6—46	6—46	6—48
Reflections measured	$h\,k \pm l$	$\pm h\,k\,l$	$\pm h\,k\,l$
Unique total data	2 169	3 937	3 065
Unique observed data	1 463 [$I > 3\sigma(I)$]	2 274 [$I > 2\sigma(I)$]	1 845 [$I > 3\sigma(I)$]
No. of variables	175	304	205
Over-determination ratio	8.4	7.5	9.0
Max. shift/error on last cycle	0.2	0.2	0.1
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.046	0.041	0.040
$R' = \Sigma w^{\frac{1}{2}}\|\Delta F\|/\Sigma w^{\frac{1}{2}}\|F_o\|$			0.040
Goodness of fit = $[\Sigma w\|\Delta F\|^2/(N_o - N_v)]^{\frac{1}{2}}$[e]			1.51

[a] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25—30 carefully centred reflections chosen from diverse regions of reciprocal space. [b] $(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]°$; $\Delta\theta = [(\lambda\alpha_2 - \lambda\alpha_1)/\lambda]\tan\theta$. [c] Graphite monochromated Mo-K_α (λ = 0.710 69 Å). [d] Niobium-filtered Mo-K_α (λ = 0.710 69 Å). [e] N_o = Number of observations, N_v = number of variables.

(Found: C, 64.35; H, 5.00; Co, 27.35; N, 3.35. Calc. for $C_{23}H_{21}Co_2N$: C, 64.35; H, 4.90; Co, 27.50; N, 3.25%). Proton n.m.r. (C_6D_6): δ 4.06 (s, CH_2), 4.60 (s, cp), and 7.43 (m, Ph).

Determination of the Structures.—Crystal data for complexes (**2**)—(**4**) are listed in Table 1. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. The reduced cells quoted were obtained with the use of TRACER.[7] For the intensities and background, individual reflection profiles[8] were analysed for (**3**), while the three-point technique was used for (**2**) and (**4**). The structure amplitudes were obtained after the usual Lorentz and polarization corrections[9] and the absolute scale was established by the Wilson method.[10] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected for complex (**3**) but not for complexes (**2**) and (**4**), so the data of these were corrected for absorption following a semi-empirical method.[11] The function minimized during least-squares refinement was $\Sigma w|\Delta F|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. At the end of the refinement the values for k and g were 1.2380 and 0.000 08 respectively for complex (**4**); unit weights were used for complexes (**2**) and (**3**) since these gave a satisfactory analysis of variance.[9] Anomalous scattering corrections were included in all structure factor calculations.[12b] Scattering factors for neutral atoms were taken from ref. 12*a* for non-hydrogen atoms and from ref. 13 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. Solution and refinement were based on the observed reflections (Table 1).

The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was carried out first isotropically, then anisotropically for non-H atoms, by 'blocked' full-matrix least squares for the three complexes. During the refinement of complex (**2**) the appearance in a difference density map of several peaks near the one independent cp ring indicated the presence of disorder. It was solved by considering the ring statistically distributed over two positions (A and B) having the same occupancy factor (0.5). These 'partial' atoms were refined isotropically. For complexes (**3**) and (**4**) the cyclopentadienyl and phenyl rings were refined as regular pentagons (C–C 1.42 Å) and hexagons (C–C 1.39 Å) respectively. For the three complexes all the hydrogen atoms other than those associated with the disordered ring in complex (**2**) were located from Fourier difference maps and introduced in the subsequent refinement as fixed atom contributions with isotropic U_{iso} fixed at 0.08 Å^2. The final difference maps showed no unusual features, with no significant peak above the general background.

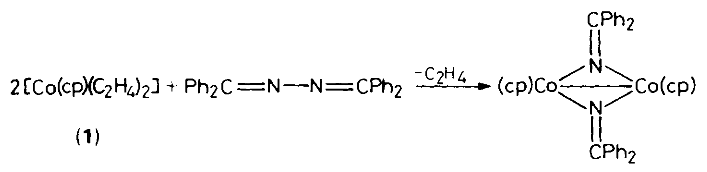
Final atomic co-ordinates for complexes (**2**)—(**4**) are listed in Tables 2—4 for non-H atoms and selected bond distances and angles are given in Tables 5—7.

Additional material available from the Cambridge Crystallographic data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The reaction of complex (**1**) with a >C=N– group is very variable depending on the substituents at the organic functionality, since they determine the site of higher reactivity.

The reaction we carried out between benzophenone azine and (**1**) gave, under very mild conditions, complex (**2**) and loss of ethylene [equation (1)]. Complex (**2**), which is diamagnetic, derives from the usual oxidative addition of the N–N bond to a 14 v.e. cobalt(I). The dimer, which contains cobalt(II), has a metal–metal bond required by its diamagnetism and confirmed by the *X*-ray analysis [Co–Co′, 2.335(1) Å]. The crystal structure consists of the packing of eight dimeric molecules in the unit cell. The space group *Fdd*2 requires the two halves of the bridged dimer to be related by the two-fold axis (see Figure 1). The co-ordination around each cobalt atom is distorted



$$2[\mathrm{Co(cp)(C_2H_4)_2}] + \mathrm{Ph_2C{=}N{-}N{=}CPh_2} \xrightarrow{-\mathrm{C_2H_4}} \mathrm{(cp)Co(\mu\text{-}N{=}CPh_2)_2Co(cp)} \quad (1)$$

(1) (2)

Table 2. Fractional atomic co-ordinates (× 10^4) for complex (2)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Co	217(1)	279(1)	0	C(25)	2 810(5)	398(3)	2 245(19)
N(1)	622(4)	−102(2)	1 029(8)	C(26)	2 341(6)	136(3)	1 755(12)
C(6)	1 129(4)	−175(2)	2 001(9)	C(1A)	968(13)	687(7)	−166(37)
C(11)	1 187(5)	−508(2)	2 780(10)	C(2A)	1 022(13)	445(5)	−1 617(35)
C(12)	567(5)	−682(2)	3 245(11)	C(3A)	296(23)	456(7)	−2 436(35)
C(13)	627(7)	−990(3)	4 049(14)	C(4A)	−120(10)	681(6)	−1 523(33)
C(14)	1 301(8)	−1 127(3)	4 376(14)	C(5A)	338(19)	814(5)	−184(36)
C(15)	1 926(7)	−956(3)	3 955(14)	C(1B)	1 101(10)	568(6)	−766(34)
C(16)	1 875(5)	−642(2)	3 159(11)	C(2B)	696(10)	411(5)	−2 197(34)
C(21)	1 653(4)	101(2)	2 479(12)	C(3B)	11(14)	559(7)	−2 100(34)
C(22)	1 451(5)	325(3)	3 654(11)	C(4B)	−9(14)	788(5)	−678(34)
C(23)	1 910(7)	593(3)	4 118(14)	C(5B)	679(21)	773(7)	236(31)
C(24)	2 586(9)	617(3)	3 431(16)				

The site occupation factor for the C(1A)—C(5B) disordered carbon atoms is 0.5.

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (3)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Co(1)	2 194(1)	1 155(1)	942(1)	C(17)	1 752(7)	2 095(2)	161(7)
Co(2)	−336(1)	1 042(1)	316(1)	C(18)	3 202(4)	2 133(2)	155(6)
O(1)	−66(4)	1 656(1)	205(5)	C(19)	4 157(4)	2 409(2)	1 083(6)
N(1)	1 308(5)	1 707(2)	350(6)	C(20)	5 554(4)	2 433(2)	1 099(6)
N(2)	890(5)	942(2)	−653(5)	C(21)	5 996(4)	2 181(2)	186(6)
C(1)	2 869(5)	851(2)	2 828(5)	C(22)	5 041(4)	1 905(2)	−742(6)
C(2)	3 480(5)	1 277(2)	2 960(5)	C(23)	3 644(4)	1 881(2)	−758(6)
C(3)	4 323(5)	1 300(2)	2 091(5)	C(31)	−544(4)	763(1)	−2 973(4)
C(4)	4 233(5)	888(2)	1 421(5)	C(32)	−742(4)	406(1)	−3 861(4)
C(5)	3 334(5)	611(2)	1 876(5)	C(33)	−2 013(4)	358(1)	−4 926(4)
C(6)	−893(5)	765(2)	1 942(4)	C(34)	−3 087(4)	667(1)	−5 104(4)
C(7)	−726(5)	437(2)	1 028(4)	C(35)	−2 890(4)	1 024(1)	−4 216(4)
C(8)	−1 715(5)	524(2)	−282(4)	C(36)	−1 618(4)	1 072(1)	−3 151(4)
C(9)	−2 492(5)	905(2)	−179(4)	C(37)	819(6)	816(2)	−1 854(7)
C(10)	−1 985(5)	1 054(2)	1 196(4)	C(38)	2 111(4)	718(2)	−2 210(5)
C(11)	865(5)	2 494(1)	−117(5)	C(39)	2 446(4)	968(2)	−3 192(5)
C(12)	−168(5)	2 569(1)	495(5)	C(40)	3 648(4)	868(2)	−3 538(5)
C(13)	−952(5)	2 957(1)	227(5)	C(41)	4 514(4)	519(2)	−2 902(5)
C(14)	−702(5)	3 270(1)	−653(5)	C(42)	4 178(4)	269(2)	−1 920(5)
C(15)	331(5)	3 195(1)	−1 264(5)	C(43)	2 976(4)	368(2)	−1 574(5)
C(16)	1 114(5)	2 807(1)	−996(5)				

Table 4. Fractional atomic co-ordinates (× 10^4) for complex (4)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Co(1)	4 041(1)	2 190(1)	1 485(0)	C(11)	6 526(3)	3 072(4)	810(2)
Co(2)	5 663(1)	156(1)	1 355(0)	C(12)	7 354(3)	3 653(4)	1 301(2)
N(1)	5 392(4)	2 068(5)	901(2)	C(13)	8 492(3)	4 608(4)	1 222(2)
C(1)	2 950(9)	4 196(8)	1 653(2)	C(14)	8 802(3)	4 983(4)	653(2)
C(2)	2 289(9)	2 843(8)	1 858(2)	C(15)	7 974(3)	4 402(4)	163(2)
C(3)	3 233(9)	2 101(8)	2 291(2)	C(16)	6 836(3)	3 447(4)	241(2)
C(4)	4 478(9)	2 997(8)	2 353(2)	C(17)	4 312(5)	1 898(7)	391(2)
C(5)	4 303(9)	4 292(8)	1 959(2)	C(18)	3 200(5)	1 020(7)	675(2)
C(6)	6 284(5)	−2 136(5)	1 461(3)	C(19)	1 768(6)	1 097(8)	470(3)
C(7)	6 106(5)	−1 454(5)	2 018(3)	C(20)	881(6)	97(10)	708(3)
C(8)	7 053(5)	−182(5)	2 111(3)	C(21)	1 352(7)	−1 022(10)	1 144(3)
C(9)	7 816(5)	−77(5)	1 611(3)	C(22)	2 716(6)	−1 069(8)	1 355(3)
C(10)	7 341(5)	−1 285(5)	1 209(3)	C(23)	3 713(6)	−57(7)	1 129(2)

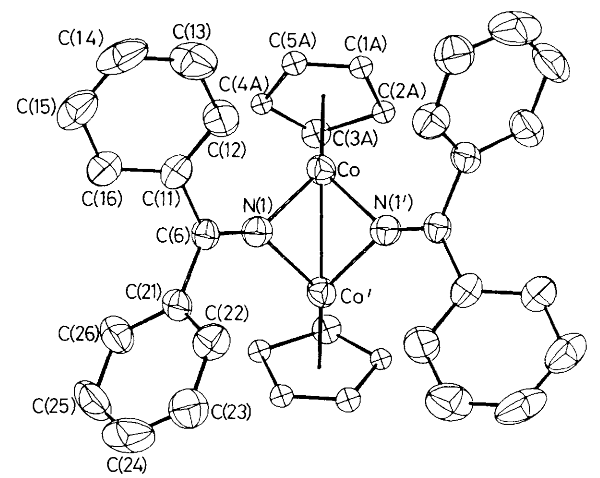


Figure 1. An ORTEP drawing for complex (**2**) (30% probability ellipsoids). For clarity only one position of the disordered cp ring is drawn

Table 5. Selected bond distances (Å) and angles (°) for complex (**2**)

Co–Co'	2.335(1)	N(1)–C(6)	1.268(10)
Co–N(1)	1.881(8)	C(6)–C(11)	1.467(11)
Co–N(1')	1.896(7)	C(6)–C(21)	1.504(11)
Co–cp(1A)	1.73(3)	Co–cp(1B)	1.71(3)
Co–C(1A)	2.12(3)	Co–C(1B)	2.08(3)
Co–C(2A)	2.11(3)	Co–C(2B)	2.10(3)
Co–C(3A)	2.15(3)	Co–C(3B)	2.11(3)
Co–C(4A)	2.12(3)	Co–C(4B)	2.13(3)
Co–C(5A)	2.12(3)	Co–C(5B)	2.13(3)
N(1)–Co–N(1')	79.7(3)	Co–N(1)–C(6)	139.6(6)
Co–N(1)–Co'	76.4(3)	Co–N(1')–C(6')	143.4(7)
cp(1A)–Co–N(1)	138.7(10)	cp(1B)–Co–N(1)	138.7(10)
cp(1A)–Co–N(1')	141.6(9)	cp(1B)–Co–N(1')	141.1(9)
N(1)–C(6)–C(11)	122.6(7)	N(1)–C(6)–C(21)	118.5(7)

Primed atoms are located at $-x$, $-y$, z; cp refers to the centroid of the cyclopentadienyl ring; A and B refer to the two positions of the disordered ring.

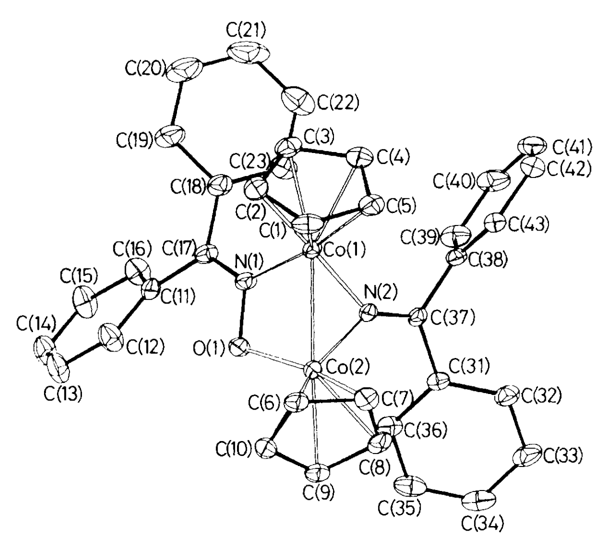


Figure 2. An ORTEP drawing for complex (**3**) (30% probability ellipsoids)

trigonal involving the cyclopentadienyl ring (considered as a unidentate ligand) and the bridging nitrogen atoms (Table 5). The two symmetry-related co-ordination planes form a dihedral angle of 72.5(8)°. The geometry of the dimer is close to those observed in similar complexes,[14] *i.e.* in $[Co_2(cp)_2(\mu\text{-NO})_2]$[15] and $[Co_2(cp)_2(\mu_2\text{-Bu}^tNCONBu^t)]$,[16] as far as the Co–C and Co–N bond distances and the Co–N–Co angles are concerned, while it shows a remarkable narrowing of the N–Co–N angle [79.7(3)°] and a tetrahedral distortion of the Co_2N_2 four-membered ring (from -0.428 to 0.428 Å). This could be due either to a stronger metal–metal interaction [2.335(1) Å] or to the bulky substituents at the imino carbon. The cp ring was found to be statistically distributed over two positions denoted A and B, which are coplanar [dihedral angle 1.8(8)°] and rotated from each other by about 21°. They are perpendicular with respect to the co-ordination plane [average dihedral angle 88.1(8)°]. The geometry of the Co(cp) unit is as usual. Other structural features are: (*i*) the N–C distance [1.268(10) Å] maintains essentially a double bond character in agreement with the i.r. spectrum showing the imino band at 1 595 cm^{-1}; (*ii*) the metal atom is remarkably out of the N(1)C(6)C(11)C(21) mean plane [0.251(1) Å]; (*iii*) the phenyl rings, forming a dihedral angle of 71.3(3)°, are rotated by 37.3(3) and 83.9(3)° respectively around the C(6)–C(11) and C(6)–C(21) bonds. The structural parameters are therefore consistent with the lack of any π delocalization within the system bridging the two metal atoms.

The reaction of complex (**1**) with a different derivative of benzophenone had the purpose both to explore the change in the reactivity of the C=N functionality and to verify whether there is any possibility to reverse the tautomeric equilibrium from the oxime form to the nitroso form[17] in the case of benzophenone oxime. The reaction led to the quite unexpected result reported in equation (2). Once again it seems that the C=N group is only marginally involved since the metal site apparently reacts at the O–H and N–O bonds. The metal does not induce any migration of the hydrogen to the carbon. A plausible mechanism for the formation of (**3**) is given in the Scheme. It requires the fundamental steps: (*i*) oxidative addition of O–H to cobalt(I); (*ii*) addition of the hydrido group to the imino functionality; (*iii*) dehydration of the hydroxylamine derivative (**B**).

Complex (**3**) is a diamagnetic cobalt(II) complex having a metal–metal bond [2.426(1) Å], as confirmed by the *X*-ray analysis. The crystal structure is reported in Figure 2. In the binuclear complex the two Co(cp) units are bridged by the oxygen and nitrogen atoms from a deprotonated benzophenone oxime molecule and by the nitrogen atom from a diphenylimido residue. This results in a five-membered bimetallic ring folded along the Co(1)–Co(2) bond by 101.7(2)°, the folding angle being defined as the dihedral angle between the

(**1**)

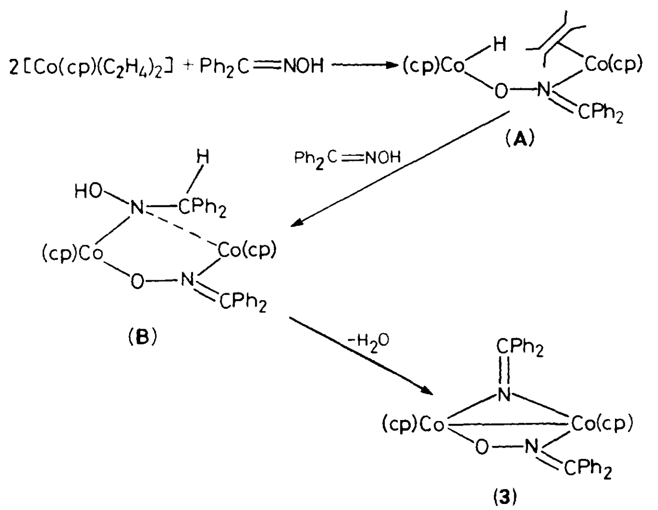
(**3**)

(2)

Table 6. Selected bond distances (Å) and angles (°) for complex (**3**)

Co(1)–Co(2)	2.426(1)	Co(2)–O(1)	1.897(3)
Co(1)–N(1)	1.906(5)	Co(2)–N(2)	1.844(6)
Co(1)–N(2)	1.857(4)	Co(2)–cp(2)	1.706(6)
Co(1)–cp(1)	1.706(5)	Co(2)–C(6)	2.112(5)
Co(1)–C(1)	2.065(5)	Co(2)–C(7)	2.067(5)
Co(1)–C(2)	2.100(4)	Co(2)–C(8)	2.054(5)
Co(1)–C(3)	2.122(4)	Co(2)–C(9)	2.092(5)
Co(1)–C(4)	2.101(5)	Co(2)–C(10)	2.128(5)
Co(1)–C(5)	2.064(5)	C(11)–C(17)	1.476(7)
O(1)–N(1)	1.343(6)	C(17)–C(18)	1.458(8)
N(1)–C(17)	1.299(8)	C(31)–C(37)	1.484(6)
N(2)–C(37)	1.280(9)	C(37)–C(38)	1.485(8)
N(1)–Co(1)–N(2)	84.4(2)	cp(1)–Co(1)–N(1)	84.4(2)
O(1)–Co(2)–N(2)	89.8(2)	cp(1)–Co(1)–N(2)	140.0(3)
Co(2)–O(1)–N(1)	105.5(3)	cp(2)–Co(2)–O(1)	132.9(2)
Co(1)–N(1)–O(1)	106.7(4)	cp(2)–Co(2)–N(2)	135.3(3)
Co(1)–N(2)–Co(2)	81.9(2)	Co(1)–N(2)–C(37)	140.2(5)
O(1)–N(1)–C(17)	118.4(5)	Co(2)–N(2)–C(37)	137.7(5)
Co(1)–N(1)–C(17)	134.7(5)		

cp(1) and cp(2) refer to the centroids of the C(1)—C(5) and C(6)—C(10) cyclopentadienyl rings respectively.



Scheme.

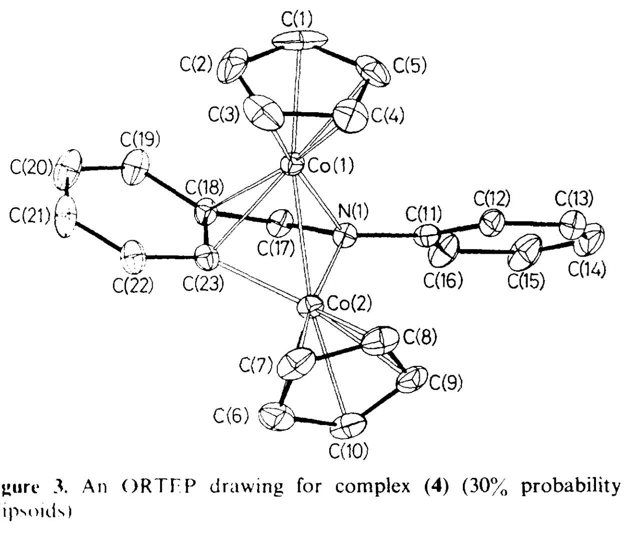
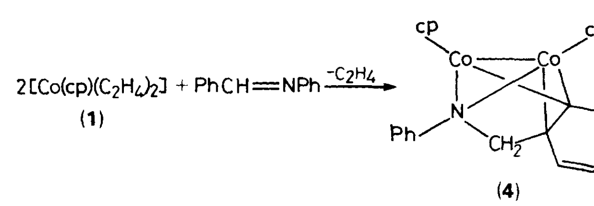


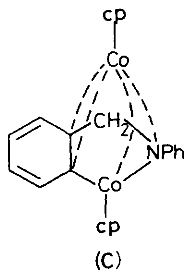
Figure 3. An ORTEP drawing for complex (**4**) (30% probability ellipsoids)



(3)

Co(1)N(1)O(1)Co(2) and Co(1)N(2)Co(2) planes. All the distances within the ring are consistent with single bonds. The Co–N bond distances and the N–Co–N and Co–N–Co bond angles within the moiety bridged by the diphenylimido group are close to those found in complex (**2**), although the formation of a larger ring causes a significant lengthening of the metal–metal bond (Table 6). In addition, the N(2)–C(37) distance [1.280(9) Å] has essentially a double-bond character; the metal atoms are markedly out of the N(2)C(37)C(31)C(38) mean plane [0.307(1) and −0.177(1) Å for Co(1) and Co(2) respectively]. The cp rings are nearly perpendicular [dihedral angles 89.0(2) and 84.6(2)°] with respect to the respective co-ordination planes through N(1)N(2)cp(1) and N(1)N(2)cp(2) from which Co(1) and Co(2) are significantly displaced by 0.069(1) and 0.140(1) Å. The two phenyl rings, which are nearly orthogonal [dihedral angle 84.5(1)°], are twisted with respect to the N(2)C(37)C(31)C(38) plane, the torsion angles around the C(37)–C(31) and C(37)–C(38) bonds being 41.2(2) and 63.7(2)° respectively. The geometry of the oxime ligand is as expected, the N–O and N–C distances [1.343(6) and 1.299(8) Å] having mainly single- and double-bond character respectively. The oxygen atom does not lie in the plane of the respective NC_3 group, being 0.138(5)° out, neither do the two metal atoms [−0.235(1) and 0.370(1) Å for Co(1) and Co(2) respectively]. The two phenyl rings are still approximately perpendicular to each other [dihedral angle 78.3(2)°], and are twisted around the C(17)–C(11) and C(17)–C(18) bonds by 33.9(2) and 58.9(2)° respectively. The structural parameters and the bridging mode of the two bridging ligands are very close to those found in $[Fe_2(CO)_6(\mu\text{-}Me_2C{=}NO)(\mu\text{-}Me_2CHNH)]$ formed in the reaction between $[Fe_3(CO)_{12}]$ and 2-nitropropane.[18]

In order to involve the C=N double bond in the reaction with the metal, we treated complex (**1**) with PhCH=NPh. The result of the reaction is given in equation (3). Complex (**4**) is a diamagnetic cobalt(II) binuclear complex having a cobalt–cobalt bond [2.375(1) Å]. All the analytical and spectroscopic data are in agreement with the structure (Figure 3) assigned on the basis of the *X*-ray analysis. It can be viewed as the metallacycle (**C**) capped by a [Co(cp)] unit. Such a view may be suggestive of its genesis too. Complex (**4**) is formed in a later stage of the reaction between (**1**), a source of the [Co(cp)] fragment, and the preformed metallacycle (**C**). The intermediate (**C**) may form *via* a sort of *o*-metallation of PhCH=NPh, which does not involve any electrophilic attack on the phenyl ring, but rather the oxidative addition of the C–H bond to the metal to give (**D**). The hydrogen atom transfer to the C=N functionality is probably a very easy process leading to (**C**) [equation (4)].

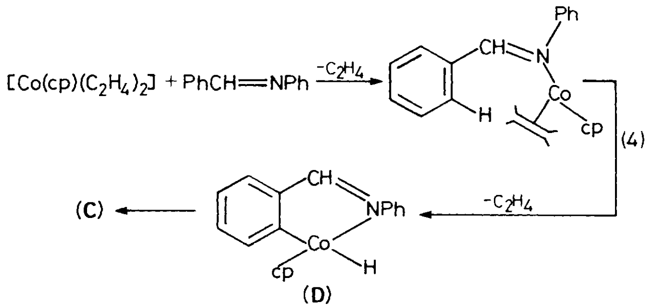


(C)

Table 7. Selected bond distances (Å) and angles (°) for complex (**4**)

Co(1)–Co(2)	2.375(1)	Co(2)–N(1)	1.929(4)
Co(1)–N(1)	1.960(5)	Co(2)–C(23)	1.914(5)
Co(1)–C(18)	2.178(5)	Co(2)–cp(2)	1.690(5)
Co(1)–C(23)	2.090(6)	N(1)–C(11)	1.424(5)
Co(1)–cp(1)	1.683(6)	N(1)–C(17)	1.485(6)
Co(1)–C(1)	2.064(7)	Co(2)–C(6)	2.050(4)
Co(1)–C(2)	2.049(8)	Co(2)–C(7)	2.050(6)
Co(1)–C(3)	2.066(6)	Co(2)–C(8)	2.088(6)
Co(1)–C(4)	2.091(5)	Co(2)–C(9)	2.112(5)
Co(1)–C(5)	2.089(6)	Co(2)–C(10)	2.088(5)
C(17)–C(18)	1.510(7)	C(18)–C(19)	1.417(7)
C(18)–C(23)	1.427(7)	C(20)–C(21)	1.414(10)
C(19)–C(20)	1.359(10)	C(22)–C(23)	1.427(8)
C(21)–C(22)	1.358(9)		
N(1)–Co(2)–C(23)	81.9(2)	Co(1)–N(1)–Co(2)	75.3(2)
C(23)–C(18)–C(17)	114.8(4)	Co(2)–C(23)–C(18)	113.1(4)
C(17)–N(1)–Co(2)	112.5(3)	C(18)–C(17)–N(1)	100.8(4)
Co(2)–N(1)–C(11)	121.4(3)	cp(2)–Co(2)–N(1)	142.1(2)
C(11)–N(1)–C(17)	115.8(4)	cp(2)–Co(2)–C(23)	134.9(2)
N(1)–C(17)–C(18)	100.8(4)	C(20)–C(21)–C(22)	119.8(6)
C(17)–C(18)–C(19)	123.4(5)	C(21)–C(22)–C(23)	121.5(6)
C(17)–C(18)–C(23)	114.8(4)	C(22)–C(23)–C(18)	116.8(5)
C(19)–C(18)–C(23)	121.5(5)	Co(2)–C(23)–C(22)	130.1(4)
C(18)–C(19)–C(20)	118.2(6)	N(1)–C(11)–C(12)	119.1(4)
C(19)–C(20)–C(21)	122.1(6)	N(1)–C(11)–C(16)	120.9(3)

cp(1) and cp(2) refer to the centroids of the C(1)—C(5) and C(6)—C(10) cyclopentadienyl rings respectively.



The incoming [Co(cp)] undergoes interaction with nitrogen, cobalt, and a C=C double bond of the benzene ring. The structural parameters (Table 7) support the description of the structure as discussed above: (*i*) the short Co(2)–C(23) bond distance [1.914(5) Å] corresponds well to a single σ bond, while the rather long Co(1)–C(18) and Co(1)–C(23) distances [2.178(5) and 2.090(6) Å] are in agreement with a cobalt–carbon asymmetric η^2 interaction; (*ii*) the trend of the C–C bond distances in the C(18)—C(23) benzene ring shows a lengthening of the C(18)–C(23), C(18)–C(19), C(20)–C(21), and C(22)–C(23) bonds [mean 1.421(7) Å] and a remarkable localization of the double bond for C(19)–C(20) and C(21)–C(22) [mean 1.358(9) Å]; (*iii*) the cobalt–nitrogen bond distances [Co(1)–N(1) 1.960(5), Co(2)–N(1) 1.929(4) Å], even if significantly different, fall in the range of values usually found for a single bond; (*iv*) the N(1)–C(17) and C(17)–C(18) distances [1.485(6) and 1.510(7) Å] are definitely single bonds in agreement with the direct localization of the hydrogen attached to C(17). In addition, the best plane through the N(1)Co(2)C(23)C(18)C(17) metallacycle is nearly parallel to the C(1)—C(5) ring of the 'incoming' Co(1)(cp) unit. However, the metallacycle, far from being planar, shows an envelope conformation with N(1) at 0.597(4) Å from the plane through the other four atoms. From Tables 5—7 and Figures 1—3, it can be seen that the $Co_2(cp)_2$ binuclear units have similar geometries in all the three complexes even as far as the mutual orientation of the two cp rings is concerned, the dihedral angle between them being 111.6(8), 96.0(2), and 107.8(2)° for (**2**), (**3**), and (**4**) respectively.

The results reported on the reactivity of the 14 v.e. species [Co(cp)] thermally generated from $[Co(cp)(C_2H_4)_2]$ with imino groups show the versatility of such a metallic fragment in cleaving N–H, O–H, and C–H bonds. In addition, due to its high unsaturation, it can establish bonds even with poorly ligating molecules. The primary product of the reaction is usually further complexed by the [Co(cp)] unit, a process which leads to a variety of polymetallic aggregates [equation (5)]. It is

$$\underset{(1)}{[Co(cp)(C_2H_4)_2]} + L \xrightarrow{-C_2H_4} [Co(cp)L] \xrightarrow[-C_2H_4]{(1)} [\{Co(cp)\}_nL] \quad (5)$$

important to emphasize that in the polynuclear structure the substrate L experiences interaction with a polymetallic skeleton.

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References

1 (*a*) H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 248; 1978, **17**, 505; (*b*) H. Werner, *ibid.*, 1983, **22**, 927; (*c*) K. Jonas, *ibid.*, 1985, **24**, 295.

2 (*a*) K. P. C. Vollhardt, *Acc. Chem. Res.*, 1977, **10**, 1; H. Simon, J. Bader, H. Günther, S. Neumann, and J. Thanos, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 539; (*b*) J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, and V. W. Day, *J. Am. Chem. Soc.*, 1979, **101**, 2768; (*c*) B. Eaton, J. M. O'Connor, and K. P. C. Vollhardt, *Organometallics*, 1986, **5**, 394; (*d*) K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1986, **108**, 856, 2091, 3150; *Organometallics*, 1986, **5**, 394.

3 K. Jonas, E. Deffense, and D. Haberman, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 716.

4 S. Stella, C. Floriani, A. Chiesi-Villa, and C. Guastini, *New J. Chem.*, 1988, **12**, 621.

5 S. Stella, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 68.

6 S. Gambarotta, S. Stella, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1987, 1789.

7 S. L. Lawton and R. A. Jacobson, TRACER, a cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, 1965.

8 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.

9 G. Sheldrick, SHELX 76, System of Crystallographic Computer Programs, University of Cambridge, 1976.

10 A. J. C. Wilson, *Nature (London)*, 1942, **150**, 151.

11 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) p. 99, (*b*) p. 149.

13 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

14 R. D. Kemmitt and D. R. Russell, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 5, ch. 34.

15 I. Bernal, J. D. Korp, G. M. Reisner, and W. A. Herrmann, *J. Organomet. Chem.*, 1977, **139**, 321.

16 Y. Matsuura, N. Yasuoka, T. Ueki, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 881.

17 S. Stella, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1988, 545.

18 S. Aime, L. Milone, R. Rossetti, and P. L. Stanghellini, *J. Chem. Soc., Chem. Commun.*, 1976, 370.

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