# Cobalt Metallacycles. Part 14.[1] Facile Transformation of $\eta^4$-Diene Complexes to Metallacyclopentenes. Preparation and Molecular Structures of $[Co(\eta^5-C_5H_5)\{\eta^4-PhNC{=}C(Ph)C(Ph){=}CNPh\}]$ and $[Co\{C({=}NR)C(Ph)C(Ph)C({=}NR)\}(\eta^5-C_5H_5)(CNC_6H_3Me_2-2,6)]$ $(R = C_6H_3Me_2-2,6)$†

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The reaction of $[Co(\eta^5-C_5H_5)(PPh_3)(R^1C{\equiv}CR^2)]$ (**1**) ($R^1$ = Ph, $R^2$ = Ph or $CO_2Me$) with excess aryl- or t-butyl-isocyanide, $R^3NC$, gives the di-iminobutadiene complexes $[Co(\eta^5-C_5H_5)(\eta^4-R^3NC{=}C(R^1)C(R^2){=}CNR^3)]$ (**2**). Complexes (**2**) react with the ligands L (L = PhNC, $4-MeC_6H_4NC$, $2,6-Me_2C_6H_3NC$, CO, or $PMe_3$) to give the 2,5-di-iminocobaltacyclopentene complexes $[Co\{C({=}NR^3)C(R^1){=}C(R^2)C({=}NR^3)\}(\eta^5-C_5H_5)L]$ (**3**). The structures of (**2a**) ($R^1 = R^2 = R^3$ = Ph) and (**3f**) ($R^1 = R^2$ = Ph, $R^3 = 2,6-Me_2C_6H_3$, and L = $2,6-Me_2C_6H_3NC$) have been determined from *X*-ray data. Complex (**2a**) crystallizes in the monoclinic space group *Cc*, with unit-cell dimensions $a$ = 19.756(4), $b$ = 10.904(3), $c$ = 12.986(3) Å, $\beta$ = 114.44(3)°, $Z$ = 4, and $R$ = 0.055 for 2 609 independent reflections. Crystals of (**3f**) are monoclinic, space group $P2_1/n$, with $a$ = 16.362(4), $b$ = 19.119(3), $c$ = 11.952(3) Å, $\beta$ = 90.73(2)°, $Z$ = 4, and $R$ = 0.047 for 2 873 independent reflections.

Reactions of low-valent transition metals with 1,3-dienes generally yield diene complexes (**A**). In some cases, however, a metallacyclopent-3-ene (**B**) is formed (Scheme ). Wilkinson and co-workers[2] have reported the formation of Fe, Rh, and Ir metallacyclopentenes isolated by the reaction of perfluorobutadiene. Platinacyclopentenes obtained by the reaction of 2,3-dimethylbuta-1,3-diene have been described by Stone and co-workers.[3]

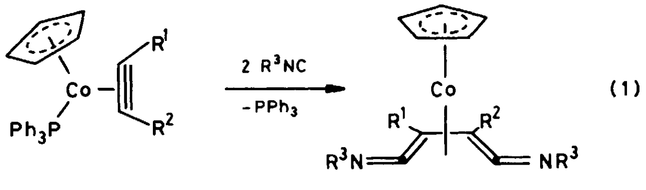
Although (**A**) could be a possible intermediate for (**B**), there has been no report on the (**A**) ——→ (**B**) conversion. Complexes of type (**A**) isolated so far appear to be too stable to undergo such a transformation. For *cis–trans* isomerization of some molybdenum–diene complexes a metallacyclopentene intermediate has been suggested.[4]

During our investigation on the reaction of alkyne complexes with isocyanides, we have encountered cobalt complexes of $\eta^4$-1,3-dienes with an imino group bonded to the 1- and 4-carbon atoms. We report herein the reaction of these cobalt complexes with additional ligands, which affords cobaltacyclopentene complexes thus realizing the (**A**) ——→ (**B**) type reaction.

A preliminary report of some of this work has been published.[5]

## Results and Discussion

*Formation of the Diene Complexes.*—Substituted acetylene complexes of cobalt, (**1**), react smoothly with two equimolar amounts of aryl- or t-butyl-isocyanide to give (**2**) [equation (1)]. Compounds (**2**) were isolated as air-stable orange crystals. Yields, elemental analyses, and some physical properties are summarized in Table 1.

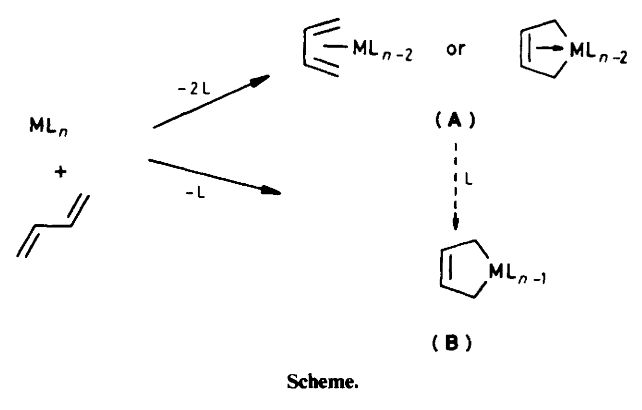


(1)

(**1a**) $R^1 = R^2$ = Ph
(**1b**) $R^1$ = Ph, $R^2 = CO_2Me$

(**2a**) $R^1 = R^2 = R^3$ = Ph
(**2b**) $R^1 = R^2$ = Ph, $R^3 = 4-MeC_6H_4$
(**2c**) $R^1 = R^2$ = Ph, $R^3 = 2-MeC_6H_4$
(**2d**) $R^1 = R^2$ = Ph, $R^3 = 2,6-Me_2C_6H_3$
(**2e**) $R^1 = R^2$ = Ph, $R^3 = Bu^t$
(**2f**) $R^1$ = Ph, $R^2 = CO_2Me$, $R^3 = 2,6-Me_2C_6H_3$

Two by-products of this reaction are 2,5-di-iminocobaltacyclopentenes, (**3**) (see later), and 1-($\eta^5$-cyclopentadienyl)-4-imino-1-(triphenylphosphine)cobaltacyclobutenes, (**4**). Complexes (**4**) result from the stabilization of an intermediate four-membered metallacycle by phosphine and their formation is a subject of the following paper.[6] Since the ratios of the isocyanide unit *vs.* acetylene unit in (**4**), (**2**), and (**3**) are 1:1, 2:1, and 3:1



**Scheme.**

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† ($\eta^5$-Cyclopentadienyl)[1—4-$\eta$-2,3-diphenyl-1,4-di(phenylimino)buta-1,3-diene]cobalt(I) and [1,4-bis(2′,6′-dimethylphenylimino)-2,3-diphenylbut-2-ene-1,4-diyl]($\eta^5$-cyclopentadienyl)(2,6-dimethylphenyl isocyanide)cobalt(III) respectively.

*Supplementary data available* (No. SUP 56491, 7 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

**Table 1.** Physical and analytical data for complexes (**2**)

| Complex | Yield (%) | M.p.[a]/°C | Analysis[b] (%) | I.r. ν(CN)/cm$^{-1}$ | δ($^1$H)[c]/p.p.m. | |
|---|---|---|---|---|---|---|
| | | | | | $C_5H_5$ | $CH_3$ |
| (**2a**) | 80 | 194—195 | C 78.15 (77.95)<br>H 4.80 (4.95)<br>N 5.50 (5.50) | 1 690[d]<br>1 715 | 4.72 | |
| (**2b**) | 79 | 196—198 | C 78.45 (78.35)<br>H 5.55 (5.45)<br>N 5.25 (5.20) | 1 695[d]<br>1 725 | 4.76 | 2.40 (6 H) |
| (**2c**) | 46 | 186—188 | C 78.10 (78.35)<br>H 5.35 (5.45)<br>N 5.25 (5.20) | 1 690[e]<br>1 725 | 4.86 | 2.40 (6 H) |
| (**2d**) | 84 | 160—161 | C 78.80 (78.75)<br>H 5.70 (5.90)<br>N 5.00 (4.95) | 1 685[d]<br>1 720 | 4.84 | 2.11 (12 H) |
| (**2e**) | 77 | 139—140 | C 74.45 (74.35)<br>H 7.05 (7.10)<br>N 5.85 (6.00) | 1 695[d]<br>1 730 | 4.88 | 1.34 (18 H) |
| (**2f**) | 30 | 143—144 | C 72.65 (72.50)<br>H 5.75 (5.70)<br>N 5.10 (5.15) | 1 690[f]<br>1 715 | 5.07 | 3.81 (3 H)<br>2.40 (6 H)<br>2.28 (6 H) |

[a] With decomposition. [b] Calculated values in parentheses. [c] In $CDCl_3$. [d] Measured in $CHCl_3$ solution. [e] Nujol mull. [f] KBr disc.

**Table 2.** Reaction conditions and physical and analytical data for complexes (**3**)

| Complex | Conditions θ/°C (time/h) | Yield % (recovered) | M.p.[a]/°C | Analysis[b] (%) | I.r./cm$^{-1}$ | δ($^1$H)[c]/p.p.m. | |
|---|---|---|---|---|---|---|---|
| | | | | | | $C_5H_5$ | $CH_3$ |
| (**3a**) | r.t. (27) | 23 (67) | 169—171 | C 78.55 (78.55)<br>H 4.75 (4.95)<br>N 6.95 (6.85) | 1 580[d]<br>1 600<br>2 120 | 4.54 | |
| (**3b**) | 70 (13) | 19 (53) | 243—244 | C 74.90 (73.95)<br>H 5.95 (5.85)<br>N 4.55 (4.80) | 1 555[e]<br>1 565 | 4.50 | 1.50 [9 H, d, *J*(PH) = 9 Hz] |
| (**3c**) | 70 (3) | 53 (31) | 170 | C 78.45 (79.00)<br>H 5.60 (5.55)<br>N 6.55 (6.45) | 1 580[d]<br>1 605<br>2 130 | 4.53 | 2.36 (3 H)<br>2.27 (6 H) |
| (**3d**) | 70 (7) | 69 (11) | 200—202 | C 79.45 (79.15)<br>H 5.55 (5.75)<br>N 6.40 (6.30) | 1 580[e]<br>1 605<br>2 200 | 4.47 | 2.39 (6 H)<br>2.26 (6 H) |
| (**3e**) | 80 (4)[f] | 79 (5) | 221—223 | C 76.85 (76.60)<br>H 4.90 (5.20)<br>N 4.90 (4.95) | 1 590[d]<br>1 605<br>2 020 | 4.62 | 2.31 (3 H) |
| (**3f**) | r.t. (5) | 97 | 215—217 | C 79.35 (79.40)<br>H 6.25 (6.10)<br>N 6.05 (6.04) | 1 582[d]<br>1 606<br>2 125 | 4.48 | 2.41 (6 H)<br>2.19 (6 H)<br>2.01 (6 H) |
| (**3g**) | r.t. (10 min) | 56 | 205—207 | C 74.50 (74.45)<br>H 6.05 (5.95)<br>N 6.25 (6.20) | 1 560[e]<br>1 600<br>1 725<br>2 200 | 4.45 | 3.62 (3 H)<br>2.41 (6 H)<br>2.26 (3 H)<br>2.18 (3 H)<br>2.04 (3 H)<br>2.01 (3 H) |

[a] With decomposition. [b] Calculated values in parentheses. [c] In $CDCl_3$. [d] Measured in $CHCl_3$ solution. [e] KBr disc. [f] CO pressure 80 atm.

respectively, the amount of these by-products largely depends on the initial molar ratio of $R^3NC$ to (**1**), the reaction time, and the substituent $R^3$ (relative reaction rate between two different isocyanides). As expected, using smaller amounts of isocyanide increases the amount of (**4**). For instance, when a four-molar excess of $4\text{-MeC}_6H_4NC$ was reacted with (**1a**) for 10 min the yields of (**2b**) and corresponding (**4**) were 79 and 1%, while the same reaction with a two-molar excess gave (**2b**) and (**4**) in 58 and 11% yields. If enough $R^3NC$ is present, a longer reaction time gives more (**3**). For example, a four-molar excess of $2,6\text{-Me}_2C_6H_3NC$ reacted with (**1a**) to give 70 and 9% yields of (**2d**) and corresponding (**3f**) in 10 min while the yields changed to 41 and 45% in a 2-h reaction.

The ν(C=N) i.r. bands are characteristic of the complexes. Complexes (**2**) show ν(C=N) at around 1 700 cm$^{-1}$ (Table 1), (**3**) at 1 550—1 600 cm$^{-1}$ (Table 2), and (**4**) at 1 610—1 630 cm$^{-1}$. The origin of these differences appears to be the degree of conjugation of the imino-group. The structure analyses have revealed (see later) that the =N– group in (**2**) does not conjugate with the butadiene moiety while those in (**3**) and (**4**)[7] are coplanar with the metallacycle plane and must be in conjugation with the unsaturated metallaring.

**Table 3.** Selected bond distances (Å) and angles (°) for (**2a**) and (**3f**) with estimated standard deviations in parentheses

(*a*) Complex (**2a**)

| | | | |
|---|---|---|---|
| Co–C(1) | 1.853(3) | C(1)–Co–C(2) | 43.0(2) |
| Co–C(2) | 2.020(4) | C(1)–Co–C(4) | 82.5(2) |
| Co–C(3) | 2.013(4) | C(2)–Co–C(3) | 41.3(2) |
| Co–C(4) | 1.843(4) | C(3)–Co–C(4) | 43.2(2) |
| Co–C(51) | 2.085(6) | Co–C(1)–C(2) | 74.8(2) |
| Co–C(52) | 2.135(5) | Co–C(4)–C(3) | 74.7(3) |
| Co–C(53) | 2.117(4) | C(1)–C(2)–C(3) | 111.1(4) |
| Co–C(54) | 2.063(5) | C(2)–C(3)–C(4) | 110.6(3) |
| Co–C(55) | 2.044(5) | C(2)–C(1)–N(11) | 135.9(4) |
| C(1)–C(2) | 1.427(5) | C(3)–C(4)–N(41) | 134.7(4) |
| C(2)–C(3) | 1.421(6) | C(1)–C(2)–C(21) | 120.7(4) |
| C(3)–C(4) | 1.429(6) | C(4)–C(3)–C(31) | 121.5(3) |
| C(1)–C(11) | 1.257(4) | | |
| C(2)–C(21) | 1.469(6) | | |
| C(3)–C(31) | 1.484(5) | | |
| C(4)–C(41) | 1.260(6) | | |

(*b*) Complex (**3f**)

| | | | |
|---|---|---|---|
| Co–C(1) | 1.964(5) | C(1)–Co–C(4) | 83.9(2) |
| Co–C(2) | 2.888(5) | C(1)–Co–C(5) | 85.8(2) |
| Co–C(3) | 2.900(5) | C(4)–Co–C(5) | 88.6(2) |
| Co–C(4) | 1.980(4) | Co–C(1)–C(2) | 112.4(3) |
| Co–C(5) | 1.788(5) | Co–C(4)–C(3) | 111.9(3) |
| Co–C(61) | 2.157(5) | Co–C(1)–N(11) | 132.3(4) |
| Co–C(62) | 2.169(5) | Co–C(4)–N(41) | 131.2(4) |
| Co–C(63) | 2.120(5) | Co–C(5)–N(51) | 177.5(4) |
| Co–C(64) | 2.120(5) | C(1)–C(2)–C(3) | 115.7(4) |
| Co–C(65) | 2.149(5) | C(2)–C(3)–C(4) | 115.1(4) |
| C(1)–C(2) | 1.498(6) | C(5)–N(51)–C(51) | 169.7(4) |
| C(2)–C(3) | 1.346(6) | | |
| C(3)–C(4) | 1.505(7) | | |
| C(1)–N(11) | 1.261(6) | | |
| C(2)–C(21) | 1.491(6) | | |
| C(3)–C(31) | 1.496(6) | | |
| C(4)–N(41) | 1.261(6) | | |
| C(5)–N(51) | 1.404(6) | | |

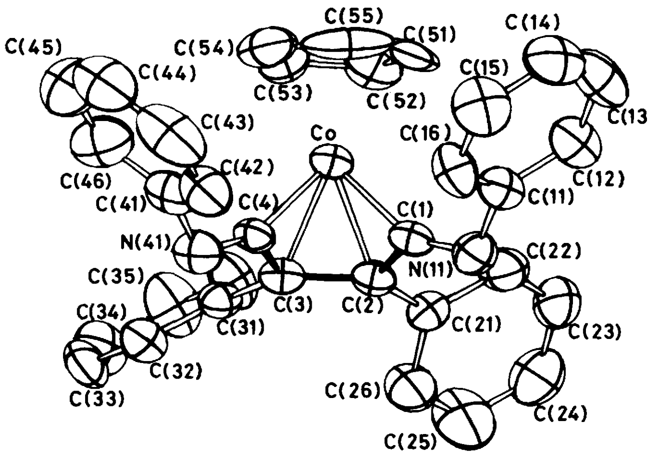


**Figure 1.** Molecular structure of complex (**2a**) showing the atomic-numbering scheme

*Molecular Structure of* (**2a**).—The structure of (**2a**) is illustrated in Figure 1 with the atomic labelling used in the corresponding Tables: selected bond lengths and angles are given in Table 3.

The cobalt atom is sandwiched between the cyclopentadienyl ring and the C(1)—C(4) plane. The dihedral angle of these two planes is 18.8(3)° (Table 4), with opening towards C(2) and C(3).

**Table 4.** Important least-squares planes and atomic deviations (Å)*

(*a*) Complex (**2a**)

Plane A: C(1), C(2), C(3), C(4)
$0.3711x + 0.2848y - 0.9582z = -3.6665$
[C(1) 0.002(2), C(2) −0.002(2), C(3) 0.003(3), C(4) −0.002(2), Co 1.389(3), N(11) −0.561(7), N(41) −0.636(7)]

Plane B: C(51), C(52), C(53), C(54), C(55)
$0.4209x + 0.5597y - 0.8241z = 1.0761$
[Co −1.722(3), C(1) −2.992(6), C(2) −3.435(5), C(3) −3.460(5), C(4) −3.044(6)]

Plane C: Co, C(1), C(4)
$0.1744x + 0.9292y + 0.2246z = 4.0891$

Plane D: C(1), N(11), C(11)
$0.7658x - 0.3661y - 0.7981z = 1.8959$

Plane E: C(4), N(41), C(41)
$0.4871x + 0.0439y + 0.5925z = 8.6948$

Interplane angles (°): A—B 18.8(3), A—C 87.6(2), A—D 49.7(4), A—E 54.7(5)

(*b*) Complex (**3f**)

Plane A: C(1), C(2), C(3), C(4)
$-0.6580x + 0.1552y + 0.7451z = 3.7996$
[Co 0.228(8), N(11) −0.099(7), N(41) −0.106(7), C(5) 1.972(8), C(21) −0.147(9), C(31) −0.007(9)]

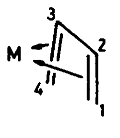
Plane B: C(61), C(62), C(63), C(64), C(65)
$0.2807x - 0.9461y - 0.1653z = -5.9519$
[Co −1.777(2), C(1) −2.940(7), C(2) −4.161(7), C(3) −4.195(7), C(4) −2.996(7)]

Plane C: C(1), N(11), C(11)
$-0.5979x + 0.1109y + 0.8014z = 4.1832$

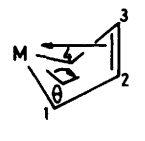
Plane D: C(4), N(41), C(41)
$0.7176x - 0.1933y - 0.6781z = -3.4949$

Interplane angles (°): A—B 116.8(3), A—C 5.4(2), A—D 5.6(5)

* *x*, *y*, and *z* are co-ordinates (Å) along the crystallographic axis.



(**C**)



(**D**)

In substituted buta-1,3-diene complexes of ($\eta^5$-cyclopentadienyl)cobalt(I), the corresponding dihedral angles are in the range 7—11°.[8] The imino planes, C(1)–N(11)–C(11) and C(4)–N(41)–C(41), have dihedral angles with the butadiene plane of 49.7(4) and 54.7(5)°, respectively. As a result of this twisting of the imino π lobe, from the normal perpendicular orientation with respect to the butadiene π lobes, the *p* lobes at C(1) and C(4) are expected to point inward to the central metal.

In 1,3-diene complexes of transition metals, the observed geometries of the diene skeletons accord with either formulation (**C**) or (**D**): generally in Group 7—10 metal–diene complexes contribution of (**C**) is dominant[8] while in Group 4 and 5 metal–diene complexes the bonding is better represented by mode (**D**).[9,10] According to the summarization by Yasuda *et al.*,[10] of

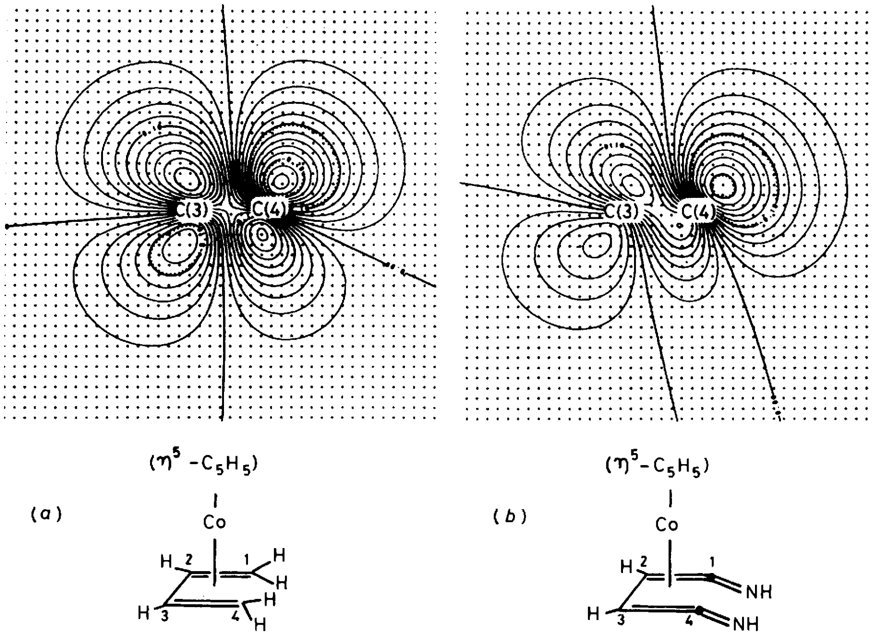


**Figure 2.** Side view of the l.u.m.o. of diene fragments along the C(3)–C(2) bond. (*a*) Butadiene fragment in [Co($\eta^5$-$C_5H_5$)($\eta^4$-$C_4H_4$)] and (*b*) di-iminobutadiene fragment in [Co($\eta^5$-$C_5H_5$){$\eta^4$-$C_4H_2(NH)_2$}]

the *X*-ray data for metal–diene complexes, the bent angle $\theta$, defined by the C(1)–M–C(4) and C(1)—C(4) diene planes, falls in the narrow range of 80—85° for Group 7—10 metal–diene complexes [type (**C**)] whereas it varies in the range 95—120° for Zr–, Hf–, and Ta–diene complexes [type (**D**)]. In addition, the difference in M–C distances, $\Delta d = \{d[\text{M–C(1)}] + d[\text{M–C(4)}]\}/2 - \{d[\text{M–C(2)}] + d[\text{M–C(3)}]\}/2$, ranges from 0 to 0.1 Å for Group 7—10 metal–diene complexes and from −0.4 to 0.0 Å for Group 4 and 5 metal complexes, *i.e.* the M–C(outer) bonds tend to be longer than the M–C(inner) bonds for type (**C**) and the reverse is true for type (**D**). Furthermore, the difference in the C–C bond lengths, defined by $\Delta l = \{l[\text{C(1)–C(2)}] + l[\text{C(3)–C(4)}]\}/2 - l[\text{C(2)–C(3)}]$, is −0.1 to 0.0 Å for Group 7—10 metal–diene complexes and 0.0 to 0.2 Å for Group 4 and 5 metal complexes. The parameters found in the present complex (**2a**), $\theta$ = 87.6° (Table 4), $\Delta d = -0.17$ Å, and $\Delta l = 0.01$ Å, are well outside the range of those for Group 7—10 metals and indicate a significant contribution of bonding mode (**D**).

Further support for the contribution of (**D**) to the structure of (**2a**) comes from the easy transformation of complexes (**2**) to the metallacyclopentene complexes (**3**) by co-ordination of additional ligands (see later), which is quite unusual for conventional metal–diene complexes. Apparently the imino groups at C(1) and C(4) are responsible for this remarkable feature. In order to elucidate the contribution of the imino group to bonding mode (**D**), the di-iminobutadiene fragment of (**2a**) and a typical butadiene fragment in ($\eta^5$-cyclopentadienyl)-cobalt–diene complexes[8] have been compared by *ab initio* molecular orbital (m.o.) calculations (STO-3G basis set; all the substituents are replaced with hydrogen for simplicity). The lowest unoccupied molecular orbital (l.u.m.o.) of the di-iminobutadiene fragment has been calculated to be 3.9 kJ mol$^{-1}$ lower in energy than the corresponding orbital of the butadiene fragment, suggesting that on complexation of these fragments to the Co($\eta^5$-$C_5H_5$) group, a greater extent of back-donation from the metal is expected for the di-iminobutadiene complex. As the importance of the diene l.u.m.o. in the bonding to the metal increases, so bonding mode (**D**) should become more significant.[11]

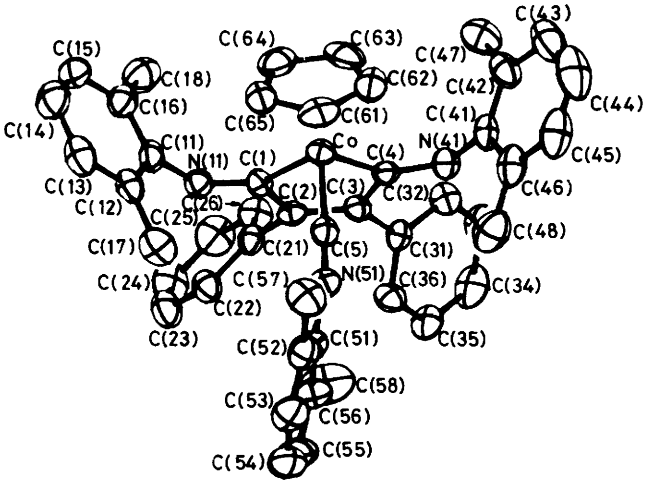
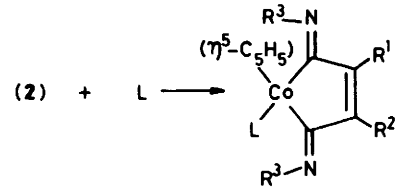


**Figure 3.** Molecular structure of complex (**3f**) showing the atomic-numbering scheme

The shape of the l.u.m.o. of the diene fragments is also different. Figure 2 illustrates the side view of the l.u.m.o. at the C(3)–C(4) bond. In the di-iminobutadiene, the *p*-lobe at C(4) is directed further outside, towards the nitrogen. Hence, to back-donate efficiently, the cobalt will shift from the normal position in [Co($\eta^5$-$C_5H_5$)($\eta^4$-$C_4H_4$)] towards the terminal carbons C(1) and C(4).

*Transformation of the Diene Complexes to Metallacyclopentenes.*—The iron complex [Fe(CNR)$_3$\{$\eta^4$-C(=NR)=C(Ph)C(Ph)=C(=NR)\}] (**5**, R = Bu$^t$), which is closely related to (**2e**), has been isolated by Stone and co-workers[12] from the reaction of [Fe(Bu$^t$NC)$_5$] with diphenylacetylene. No transformation of complex (**5**) to a metallacyclopentene has been reported. Here also, (**2e**) has not so far shown such reactivity, probably due to an electronic effect of the t-butyl group. However, other di-iminobutadiene complexes with $R^3$ = aryl react with L to form di-iminocobaltacyclopentenes (**3**) [equation (2)] which are isolated as very air-stable orange crystals. Yields, elemental analyses, and some physical properties are listed in Table 2.



(2)

(**3a**) $R^1 = R^2 = R^3 = Ph, L = PhNC$

(**3b**) $R^1 = R^2 = R^3 = Ph, L = PMe_3$

(**3c**) $R^1 = R^2 = Ph, R^3 = 4\text{-}MeC_6H_4, L = 4\text{-}MeC_6H_4NC$

(**3d**) $R^1 = R^2 = Ph, R^3 = 4\text{-}MeC_6H_4, L = 2,6\text{-}Me_2C_6H_3NC$

(**3e**) $R^1 = R^2 = Ph, R^3 = 4\text{-}MeC_6H_4, L = CO$

(**3f**) $R^1 = R^2 = Ph, R^3 = 2,6\text{-}Me_2C_6H_3, L = 2,6\text{-}Me_2C_6H_3NC$

(**3g**) $R^1 = Ph, R^2 = CO_2Me, R^3 = 2,6\text{-}Me_2C_6H_3,$
$L = 2,6\text{-}Me_2C_6H_3NC$

Among complexes (**2**) with $R^3$ = aryl, the most reactive are those with $R^3$ = 2,6-$Me_2C_6H_3$: (**2d**) and (**2f**) react smoothly with 2,6-$Me_2C_6H_3NC$ at room temperature to give (**3f**) and (**3g**) respectively, while complexes (**2**) with less bulky $R^3$ groups react only at elevated temperatures. Seemingly, bulky $R^3$ groups in (**2**) facilitate the (**2**) to (**3**) conversion by releasing some steric strain. As for the bulkiness of the entering ligand L, a smaller bulk is more favourable. While isocyanide, carbon monoxide, and trimethylphosphine react, triphenylphosphine and alkynes do not.

*X*-Ray analysis has revealed (see later) that the imino substituents in (**3**) are oriented *syn* with respect to the metal. The configuration of the C=N bond therefore does not change during the transformation. When $R^3$ = 2,6-$Me_2C_6H_3$ [(**3f**) or (**3g**)] the $^1H$ n.m.r. spectra show two different absorptions for the methyl protons of the aromatic ring (Table 2), indicating hindered rotation of $R^3$ probably due to steric interaction with the co-ordinating L.

The two imino groups in (**3**) are expected to be in conjugation with the central double bond of the metallacycle. It seems likely that the realization of the conjugated form from the unconjugated state in (**2**) is an important driving force of the reaction.

*Molecular Structure of* (**3f**).—Figure 3 shows a perspective view and the numbering scheme of complex (**3f**). Important bond lengths and angles are reported in Table 3 and some least-squares planes in Table 4.

The molecule has a 'piano stool' geometry with C(1)–Co–C(5) 85.8(2), C(4)–Co–C(5) 88.6(2), and C(1)–Co–C(4) 83.9(2)°. The metallacyclopentene framework is almost planar and in particular C(1)–C(2)–C(3)–C(4) has good planarity, the largest deviation from the best plane being 0.000 3(31) Å: the cobalt atom is displaced from this plane by 0.228(8) Å in the direction of C(5) (Table 4). The imino planes, C(1)–N(11)–C(11) and C(4)–N(41)–C(41), are almost coplanar with C(1)–C(2)–C(3)–C(4) [dihedral angles 5.4(2) and 5.6(5)°].

**Table 5.** Crystal data

| | (**2a**) | (**3f**) |
|---|---|---|
| Formula | $C_{33}H_{25}CoN_2$ | $C_{46}H_{42}CoN_3$ |
| *M* | 508.5 | 601.5 |
| Crystal size/mm | 0.40 × 0.15 × 0.10 | 0.36 × 0.24 × 0.16 |
| Space group | *Cc* | $P2_1/n$ |
| Crystal system | Monoclinic | Monoclinic |
| $a$/Å | 19.756(4) | 16.362(4) |
| $b$/Å | 10.904(3) | 19.119(3) |
| $c$/Å | 12.986(3) | 11.952(3) |
| $\beta$/° | 114.44(3) | 90.73(2) |
| $U$/Å$^3$ | 2 546.8 | 3 738.5 |
| $Z$ | 4 | 4 |
| $D_m$ (flotation)/g cm$^{-3}$ | 1.31(5) | 1.22(5) |
| $D_c$/g cm$^{-3}$ | 1.326 | 1.236 |
| $F(000)$ | 1 056 | 1 464 |
| Radiation ($\lambda$/Å) | Mo-$K_\alpha$ (0.7107) | Mo-$K_\alpha$ (0.7107) |
| $\mu$/cm$^{-1}$ | 6.9 | 4.9 |
| No. of unique reflections | 2 609 | 2 873 |
| $[(\sin\theta)/\lambda]_{max.}$ | 0.70 | 0.65 |
| $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$ | 0.055 | 0.047 |
| $R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$ | 0.024 | 0.026 |
| Max. ratio of least-squares shift-to-error | 0.6 | 0.4 |
| Maximum residual electron density (e Å$^{-3}$) | 0.82 | 0.25 |

As expected, the C(1)—C(4) framework undergoes drastic change on going from (**2**) to (**3**). In (**2a**) the three C–C bond distances are almost equal [1.421(6)—1.429(6) Å] whereas in (**3f**) a long–short–long sequence is evident [C(1)–C(2) and C(3)–C(4) 1.498(6) and 1.505(7) Å, and C(2)–C(3) 1.346(6) Å], although they are more averaged than typical C–C single and double bond lengths owing to the conjugation.

The co-ordinated isocyanide is bent back slightly, C(5)–N(51)–C(51) being 169.7(4)°. This, and the rather short Co–C(5) distance of 1.788(5) Å, suggest some back-donative character of the Co–isocyanide bond, although the central metal is formally in the +3 oxidation state.

## Experimental

All reactions were carried out under an inert atmosphere. For column chromatography, Sumitomo activated alumina KCG-30 was used. Complexes (**1a**) and (**1b**) were prepared according to the previously reported method.[13]

*Preparation of Di-iminobutadienecobalt Complexes* (**2**).—To a stirred solution of (**1a**) (282 mg, 0.5 mmol) in benzene (20 cm$^3$) was added phenyl isocyanide (155 mg, 1.5 mmol) at room temperature. After 10 min the reaction mixture was chromatographed on alumina and a yellow band eluted with benzene–MeCO(OEt) (3:1). Removal of the solvent from the eluate and crystallization from benzene–hexane gave orange crystals of (**2a**) (204 mg, 80% yield).

Complexes (**2b**), (**2c**), and (**2e**) were prepared similarly. For the preparation of (**2d**) and (**2f**) exactly two equimolar amounts of 2,6-xylyl isocyanide to (**1a**) or (**1b**) were used, otherwise considerable amounts of (**3f**) or (**3g**) were also formed.

*Preparation of* 2,5-*Di-iminocobaltacyclopentene Complexes* (**3**).—A mixture of (**2a**) (254 mg, 0.5 mmol) and phenyl isocyanide (103 mg, 1 mmol) in benzene (10 cm$^3$) was kept for 27 h at room temperature and chromatographed on alumina. The orange solution eluted by benzene was concentrated and treated with hexane to give orange crystals of (**3a**) (70 mg, 23% yield).

**Table 6.** Atomic co-ordinates ( × $10^4$) for complexes (**2a**) and (**3f**) with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| (*a*) Complex (**2a**) | | | | | | | |
| Co | 5 000(0) | 896(0) | 5 000(0) | C(26) | 5 203(3) | −2 997(4) | 5 861(4) |
| N(11) | 6 293(2) | 397(3) | 7 204(3) | C(31) | 3 767(2) | −1 078(4) | 4 756(3) |
| N(41) | 4 016(2) | 1 456(3) | 6 187(3) | C(32) | 3 142(2) | −1 016(4) | 4 987(3) |
| C(1) | 5 683(2) | 272(4) | 6 361(3) | C(33) | 2 523(2) | −1 674(4) | 4 349(4) |
| C(2) | 5 194(2) | −723(4) | 5 828(3) | C(34) | 2 490(2) | −2 400(5) | 3 470(4) |
| C(3) | 4 438(2) | −365(3) | 5 468(3) | C(35) | 3 084(3) | −2 410(5) | 3 209(4) |
| C(4) | 4 389(2) | 887(4) | 5 755(3) | C(36) | 3 722(3) | −1 765(4) | 3 838(4) |
| C(11) | 6 677(2) | 1 530(4) | 7 328(3) | C(41) | 3 960(3) | 2 745(4) | 6 176(4) |
| C(12) | 7 296(2) | 1 568(4) | 7 088(3) | C(42) | 4 409(3) | 3 448(4) | 7 080(4) |
| C(13) | 7 658(3) | 2 661(5) | 7 173(4) | C(43) | 4 280(3) | 4 708(3) | 7 045(4) |
| C(14) | 7 433(3) | 3 686(4) | 7 517(4) | C(44) | 3 737(3) | 5 244(4) | 6 165(5) |
| C(15) | 6 826(3) | 3 650(4) | 7 770(4) | C(45) | 3 290(3) | 4 551(4) | 5 300(5) |
| C(16) | 6 449(2) | 2 564(4) | 7 672(4) | C(46) | 3 389(3) | 3 301(4) | 5 298(4) |
| C(21) | 5 489(2) | −1 910(4) | 5 670(3) | C(51) | 5 728(3) | 1 606(5) | 4 359(4) |
| C(22) | 6 108(2) | −1 975(4) | 5 418(4) | C(52) | 5 252(3) | 835(5) | 3 553(3) |
| C(23) | 6 400(3) | −3 092(4) | 5 316(4) | C(53) | 4 532(2) | 1 276(4) | 3 244(3) |
| C(24) | 6 099(3) | −4 148(5) | 5 475(4) | C(54) | 4 573(3) | 2 322(4) | 3 870(4) |
| C(25) | 5 500(3) | −4 084(5) | 5 753(5) | C(55) | 5 329(3) | 2 528(4) | 4 581(4) |
| (*b*) Complex (**3f**) | | | | | | | |
| Co | 2 837(0) | 4 281(0) | 6 527(1) | C(33) | 1 905(3) | 6 837(3) | 3 224(4) |
| N(11) | 4 188(2) | 5 120(2) | 7 512(3) | C(34) | 1 701(3) | 7 435(3) | 3 801(5) |
| N(41) | 1 798(2) | 4 862(2) | 4 700(3) | C(35) | 1 792(3) | 7 465(2) | 4 939(4) |
| N(51) | 1 788(2) | 4 861(2) | 8 277(3) | C(36) | 2 104(3) | 6 892(2) | 5 531(4) |
| C(1) | 3 565(3) | 5 069(2) | 6 887(3) | C(41) | 1 376(3) | 4 250(3) | 4 369(4) |
| C(2) | 3 293(2) | 5 735(3) | 6 337(3) | C(42) | 1 626(3) | 3 911(3) | 3 385(4) |
| C(3) | 2 668(2) | 5 676(2) | 5 600(3) | C(43) | 1 179(4) | 3 332(3) | 3 019(5) |
| C(4) | 2 340(3) | 4 946(2) | 5 447(4) | C(44) | 491(4) | 3 121(3) | 3 571(5) |
| C(5) | 2 184(3) | 4 628(2) | 7 579(4) | C(45) | 244(3) | 3 465(3) | 4 498(5) |
| C(11) | 4 649(3) | 4 612(2) | 8 096(4) | C(46) | 669(3) | 4 039(3) | 4 945(4) |
| C(12) | 4 444(3) | 4 373(3) | 9 164(4) | C(47) | 2 344(3) | 4 167(3) | 2 737(4) |
| C(13) | 4 969(3) | 3 895(3) | 9 686(4) | C(48) | 399(3) | 4 389(3) | 5 990(4) |
| C(14) | 5 678(3) | 3 672(3) | 9 195(5) | C(51) | 1 429(3) | 5 125(2) | 9 251(4) |
| C(15) | 5 890(3) | 3 934(3) | 8 154(4) | C(52) | 1 174(3) | 4 635(3) | 10 050(4) |
| C(16) | 5 399(3) | 4 431(3) | 7 598(4) | C(53) | 842(3) | 4 909(3) | 11 021(4) |
| C(17) | 3 670(3) | 4 601(3) | 9 723(4) | C(54) | 770(3) | 5 619(3) | 11 170(4) |
| C(18) | 5 655(3) | 4 766(3) | 6 517(4) | C(55) | 1 015(3) | 6 090(3) | 10 353(5) |
| C(21) | 3 786(3) | 6 377(2) | 6 554(4) | C(56) | 1 334(3) | 5 845(3) | 9 354(4) |
| C(22) | 3 894(3) | 6 640(2) | 7 627(4) | C(57) | 1 284(3) | 3 860(3) | 9 874(4) |
| C(23) | 4 383(3) | 7 221(3) | 7 831(4) | C(58) | 1 562(4) | 6 345(3) | 8 438(5) |
| C(24) | 4 781(3) | 7 533(3) | 6 946(5) | C(61) | 2 673(3) | 3 205(2) | 7 021(4) |
| C(25) | 4 677(3) | 7 278(3) | 5 869(5) | C(62) | 2 462(3) | 3 269(3) | 5 880(4) |
| C(26) | 4 178(3) | 6 704(3) | 5 671(4) | C(63) | 3 157(3) | 3 514(3) | 5 328(4) |
| C(31) | 2 310(3) | 6 277(2) | 4 960(4) | C(64) | 3 798(3) | 3 584(3) | 6 125(5) |
| C(32) | 2 199(3) | 6 249(3) | 3 808(4) | C(65) | 3 499(3) | 3 395(2) | 7 174(4) |

From the second orange eluate [benzene–MeCO(OEt) (3:1)] the starting material (**2a**) was recovered (170 mg, 67%). For a better yield of (**3**) reactions were carried out at an elevated temperature (Table 2), except for (**3f**) and (**3g**) which were obtained in high yields even at room temperature.

*X-Ray Crystallographic Analyses.*—The crystal and refinement data are summarized in Table 5. *X*-Ray measurements were carried out with a Rigaku automatic four-circle diffractometer using $\omega$–$2\theta$ scans and 10-s stationary background counts made at the lower and upper limits of each scan. A constant scan speed of 0.06° $s^{-1}$ was used. Lorentz and polarization corrections were applied.

The structures were solved using three-dimensional Patterson and Fourier techniques and refined by block-diagonal least squares. The Co atom in each case was located from a Patterson map. For each complex a subsequent difference-Fourier synthesis revealed the positions of all the non-hydrogen atoms. The hydrogen atoms of the phenyl and cyclopentadienyl rings were placed in calculated positions and included in subsequent refinements with isotropic thermal parameters. Methyl protons in (**3f**) could be located from a difference Fourier map. In the final stage of refinements weights of the form $w = 1/(\sigma F_o)^2$ were applied. The standard deviation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{\frac{1}{2}}$, where $m$ and $n$ are the numbers of reflections and refined parameters respectively, was 2.47 for (**2a**) and 2.21 for (**3f**). Anomalous dispersion effects for Co were included in the calculation using $\Delta f'$ and $\Delta f''$ values from ref. 14. Atomic scattering factors were from International Tables.[15] Final atomic parameters are given in Table 6.

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