Metallacyclobutene Formation from a Substituted-acetylene Complex of Cobalt and an Isocyanide. Regioselectivity and Rearrangement

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The regioselectivity observed in the formation of the iminocobaltacyclobutenes (3) from the substituted-acetylene complex (1) and the isocyanide (2) has been shown to be due to the electronic effect of substituents on the acetylene; skeletal rearrangement of the metallacycle has proved that the complexes (3) are the kinetically controlled products.

Examples have been reported of metallacycles formed by the reaction of two unsaturated units on transition metals,[1] but the substituent effect in such reactions has not been explored although it could be fundamental to the nature of the reaction.

Theoretical analysis by Stockis and Hoffmann on $Fe(CO)_3(olefin)_2$ has shown that an electron-withdrawing substituent on the olefin occupies the α-position of the resulting ferracyclopentane.[2] We have recently reported the bis(acetylene)cobalt to cobaltacyclopentadiene transformation where the acetylene carbon bearing a bulkier substituent occupies the α-position of the metallacycle formed.[3]

We herein report a reaction (Scheme 1) in which the regioselectivity is electronically induced and kinetically controlled. The reaction of (1) and (2) in benzene solution at room temperature gave air-stable orange–brown crystals of (3) in yields of 30—80%. This reaction is analogous to the previously reported reaction of (1) with acetylenes or olefins to give co-ordinatively unsaturated metallacycles, where the intermediacy of $CpCo(acetylene)_2$ (Cp $= \eta\text{-}C_5H_5$) or CpCo(acetylene)(olefin) was proved by kinetic studies.[3,4] In the present system too, the key step of the reaction may well be the transformation of the CpCo(acetylene)(isocyanide) (4) to the metallacycle (5). The presence of (5) is supported by the observation that (3) does not react further with the isocyanide (2) at room temperature while when (1) and (2) were mixed in the usual way[5] the main product was a five-membered metallacycle, formed by inclusion of two molecules of (2). We carried out the reaction (Scheme 1) in the presence of a large excess of PPh_3 in order to stabilize (5) and so to give (3).
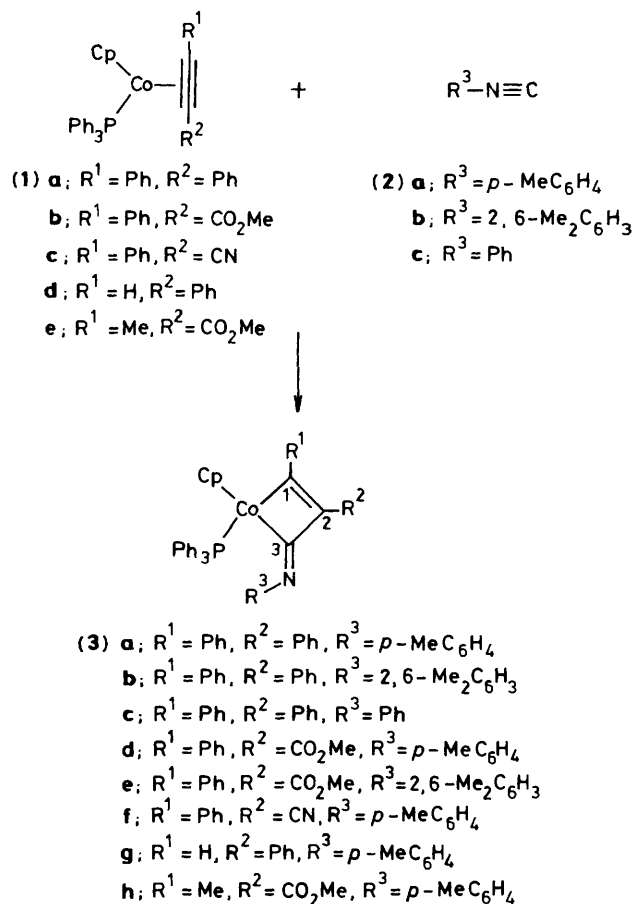
This reaction is highly regioselective as only one of the two possible regio-isomers was detected when unsymmetrical acetylenes were used. The positions of the substituents in (3d) and (3h) were determined by single crystal X-ray analyses.†

(1) a; R¹ = Ph, R² = Ph

   b; R¹ = Ph, R² = CO₂Me

   c; R¹ = Ph, R² = CN

   d; R¹ = H, R² = Ph

   e; R¹ = Me, R² = CO₂Me

(2) a; R³ = p- MeC₆H₄

   b; R³ = 2, 6-Me₂C₆H₃

   c; R³ = Ph

(3) a; R¹ = Ph, R² = Ph, R³ = p-MeC₆H₄

   b; R¹ = Ph, R² = Ph, R³ = 2,6-Me₂C₆H₃

   c; R¹ = Ph, R² = Ph, R³ = Ph

   d; R¹ = Ph, R² = CO₂Me, R³ = p-MeC₆H₄

   e; R¹ = Ph, R² = CO₂Me, R³ = 2,6-Me₂C₆H₃

   f; R¹ = Ph, R² = CN, R³ = p-MeC₆H₄

   g; R¹ = H, R² = Ph, R³ = p-MeC₆H₄

   h; R¹ = Me, R² = CO₂Me, R³ = p-MeC₆H₄

Scheme 1

Table 1. Selected structural parameters for the complexes (3d), (3h), and (6a).

	(3d)	(3h)	(6a)
		Bond length/Å	
Co–C(1)	1.968(9)	1.908(7)	1.931(5)
Co–C(3)	1.983(3)	1.991(6)	1.980(4)
C(1)–C(2)	1.338(11)	1.357(10)	1.342(6)
C(2)–C(3)	1.504(12)	1.468(10)	1.477(6)
		Bond angle/°	
C(1)–Co–C(3)	68.7(3)	68.4(3)	67.3(2)
Co–C(1)–C(2)	97.1(6)	98.5(5)	99.2(3)
Co–C(3)–C(2)	91.1(5)	91.3(4)	92.5(3)
C(1)–C(2)–C(3)	103.1(7)	101.8(5)	100.5(4)

The structural parameters for the metallacycle framework are listed in Table 1. In both (3d) and (3h) the strongly electron-withdrawing substituent, CO₂Me, was found to occupy the β-position of the metallacycle while the phenyl or methyl group becomes the α-substituent as indicated in Scheme 1. These results imply that the regioselectivity originates not from a steric effect‡ but from an electronic

‡ To the best of our knowledge a steric parameter for the CO₂Me group has not been reported, but our model study using the CPK model (ref. 6) showed the following order of bulkiness: Ph > CO₂Me > Me. Note that this is reflected in the Co–C(1) bond lengths listed in Table 1. The bond is the longest when the substituent at C(1) is Ph [(3d)] and the shortest when it is Me [(3h)].

(4') 43·1 kJ mol⁻¹

l_1 1.89 Å
l_2 1.91 Å
β 164.5°
C(1)–Co–C(3) 70.5°
Co–C(1)–C(2) 96.3°
Co–C(3)–C(2) 91.5°

(5) 20·1 kJ mol⁻¹

l_1 2.26 Å
l_2 2.17 Å
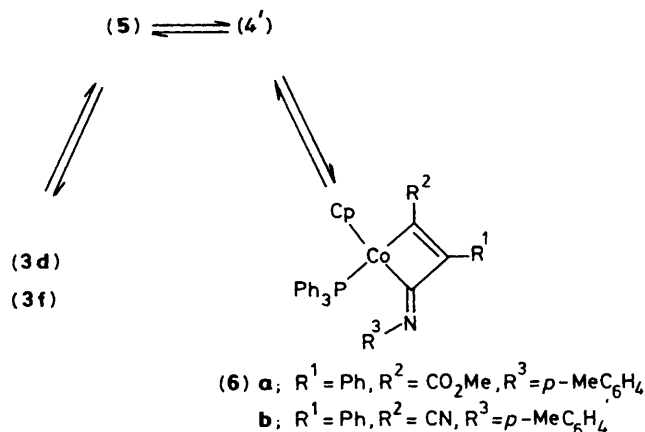l_3 1.23 Å
l_4 1.18 Å
α 97.0°

(4) 0·0 kJ mol⁻¹
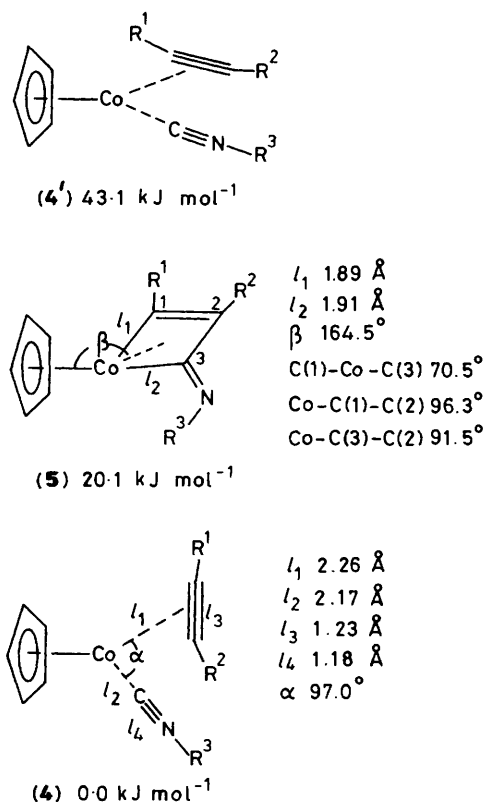
Figure 1. Calculated geometries and relative energies of the intermediates (4), (4'), and (5); R¹ = R² = R³ = H.

requirement such that the acetylenic carbon atom with an electron-withdrawing substituent becomes the β-carbon of the metallacycle and the carbon atom with an electron-donating or less electron-withdrawing substituent becomes the α-carbon.

As the phosphine-free species, (4) and (5), cannot be isolated their structures and energies were determined using *ab initio* molecular orbital calculations.§ In the calculations, the geometries of the Cp-fragment, the C–H and N–H bonds, and the C₃-framework of the metallacycle were fixed. By relaxing other geometrical parameters, the most stable forms of (4) and (5) were calculated and are illustrated in Figure 1. Product (5) is *ca.* 20 kJ mol⁻¹ higher in energy than (4) probably owing to its co-ordinative unsaturation, but in the actual system (5) may be solvent-co-ordinated. The barrier for rotation of the co-ordinated acetylene in (4) to a coplanar geometry (4') was calculated to be *ca.* 43 kJ mol⁻¹. Since the geometry of (4') resembles that of (5), it is very probable that (4') is close to the transition state. Owing to the electrophilic nature of the isocyanide carbon [C(3)] it will prefer R² to be an electron-withdrawing substituent, the polarization of the acetylenic π electrons then being C(1)^δ+≡C(2)^δ−.

That the complexes (3) are the kinetically controlled

§ The pseudo-potential method of Barthelat *et al.* (ref. 7) was employed. The program used was PSHONDO (ref. 8) which has been revised by Daudey to apply the pseudo-potential method to the original HONDO (ref. 9) program. The 4s and 4p orbitals of Co were the three-term GTO's evaluated by Topiol *et al.* (ref. 10). The 3d-valence orbitals were the five-term GTO's of Hay contracted to 2 dimensions (ref. 11). Pople's STO-4G set was used for the other atoms (ref. 12).

$(5) \rightleftharpoons (4')$

(3d)

(3f)

(6) a; R^1 = Ph, R^2 = CO_2Me, $R^3 = p$-MeC_6H_4

b; R^1 = Ph, R^2 = CN, $R^3 = p$-MeC_6H_4

Scheme 2

products was demonstrated by their rearrangement to thermodynamically stable isomers. When heated at 80 °C in benzene solution (3d) isomerized to its regioisomer (6a), the structure of which was confirmed by a single-crystal X-ray analysis (Table 1).† In order to prevent decomposition, it was essential that a molar excess of triphenylphosphine was present, and under these conditions the yield was almost quantitative. Complex (3f) also isomerizes to give (6b) but not as easily (see Scheme 2).

The isomerization of (3d) with varying amounts of triphenylphosphine was monitored by n.m.r. spectroscopy. The rate observed was first order with respect to (3d) and decreased with increasing amount of triphenylphosphine.¶ The reaction is thus unimolecular, proceeds via a phosphine-free intermediate (5), and probably via a d^8 complex (4').

To compare the thermodynamic stability of the metallacycles as a function of the position of an electron-withdrawing substituent, we made calculations on the model complexes (5;

R^1 = F, R^2 = R^3 = H) and (5; R^1 = R^3 = H, R^2 = F). The calculations revealed that (5; R^1 = F, R^2 = R^3 = H) is 20.9 kJ mol^{-1} more stable than (5; R^1 = R^3 = H, R^2 = F). This result supports a generally accepted but rather vague concept that transition metal–alkyl complexes are stabilized by an electron-withdrawing substituent. We conclude that at least part of the driving force for the rearrangement reaction (Scheme 2) originates in the thermodynamic stability of the metallacycle itself where the carbon with an electron-withdrawing substituent prefers the position next to the metal.

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¶ For example the isomerization was complete in 3 h when PPh₃ : (3) was 1.5 : 1, but when the ratio was 5 : 1 there was only 60% conversion.