Novel Double Insertion Reactions of Carbenes into the Cobalt–Carbon Bonds of a Cobalt–cyclopentadienyl Metallocycle

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The reaction $[(\eta^5\text{-}C_5H_5)\overline{Co(CMeCMeCMeC}Me)(PPh_3)]$ with α-diazo ketones results in the novel double insertion of carbene fragments to form a proposed cobaltacycloheptadiene intermediate which undergoes reductive elimination to form an η^4-coordinated triene.

The cobaltacyclopentadiene metallocycles of general formula $[(\eta^5\text{-}C_5H_5)\overline{Co(CR^1CR^2CR^3C}R^4)(PPh_3)]$ are known to undergo insertion reactions with carbon monoxide, alkenes, alkynes and isocyanides to form cyclopentadienones, cyclohexadienes, benzenes and iminocyclopentenes.[1–4] Recently the first example of a transition metal mediated coupling of two alkynes with a carbene to form a substituted η^4-cyclopentadiene cobalt complex was reported.[5] Furthermore, coupling reactions of coordinated alkynes with carbene precursors (α-diazo esters) to form butadienes have been reported.[6]

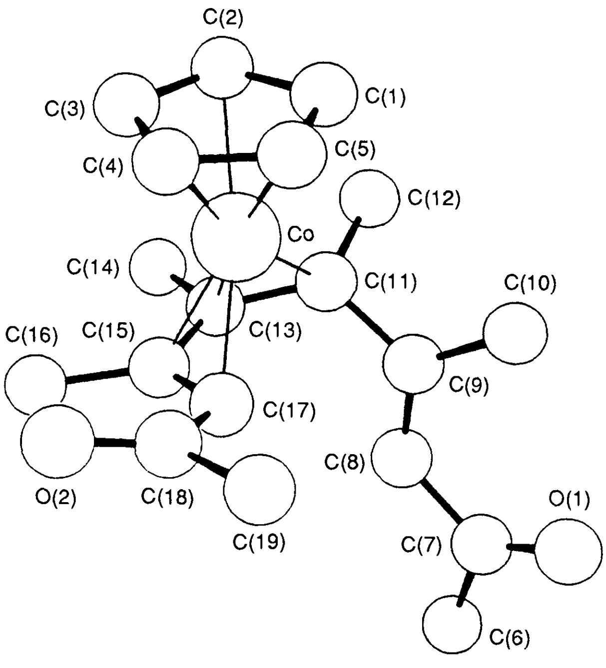
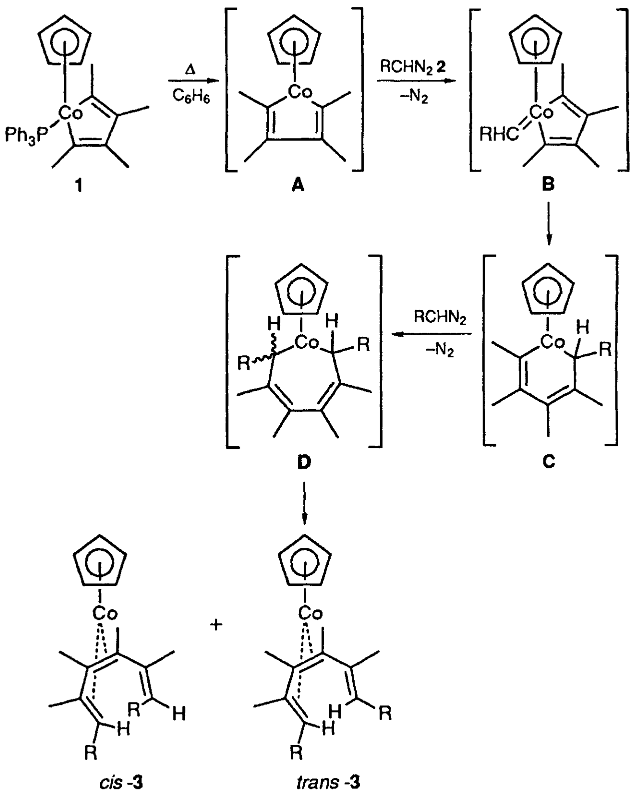


Fig. 1 Structure of *trans*-**3a**. Selected bond distances (Å): Co–C(11) 2.032(5), Co–C(13) 2.005(5), Co–C(15) 2.004(5), Co–C(17) 2.030(5), C(11)–C(13) 1.435(6), C(13)–C(15) 1.448(6), C(15)–C(17) 1.442(7), C(8)–C(9) 1.361(7), C(9)–C(11) 1.505(7).

Torsion angles (°); C(15)–C(13)–C(11)–C(9) 54.66(82), C(15)–C(13)–C(11)–C(12) −162.98(54).

Carbene insertion reactions into metallocycles are an important new area of study in which relatively little work has been done.

We report the reaction of $[(\eta^5\text{-}C_5H_5)\overline{\text{Co(CMeCMe-CMeC}}\text{Me})(PPh_3)]$ **1** on a small scale (*ca.* 1 mmol) with a sixfold excess of the α-diazo ketones $RCHN_2$ (R = MeCO **2a**, $MeCH_2CO$ **2b**, $PhCH_2CO$ **2c**) under N_2 in refluxing benzene over 5 h, resulting in low yields (*ca.* 10%) of the products $[(\eta^5\text{-}C_5H_5)Co\{\eta^4\text{-}C(CR)HCMeCMeCMeC(Me)CH(CR)\}]$ **3**. These were isolated by column chromatography† as air-stable red oils. The NMR spectra‡ of these products show a duplicated pattern of peaks, which indicates a mixture of two isomers. The product **3a** crystallised from hexane as dark-red needles (m.p. 121.5–123 °C). An X-ray diffraction study§ established the structure *trans*-**3a** for this complex (see Fig. 1).



a; R = MeCO
b; R = EtCO
c; R = $PhCH_2CO$

Scheme 1

The bonds around C(11) are considerably distorted. C(12) is 0.38 Å above the plane C(11)–C(17) while C(9) is 1.01 Å below the plane. This is due to steric interactions. The strained conformation of the triene with regard to the *cis*-arrangement about C(11)–C(13), points to a cyclic intermediate in the formation of **3a**. The structure of **3a** has a *trans*-arrangement about the uncoordinated double bond C(8)–C(9). The NMR data on the pure *trans*-**3a** as well as the isomer mixture, show an upfield shift for H(17) and a downfield shift for the H(8) resonance. This indicates that the isomer of *trans*-**3a** has a *cis*-arrangement about C(8)–C(9). This is supported by low (−50 °C, $CDCl_3$) and high temperature (65 °C, C_6D_6) NMR studies which show no merging of the resonances of the two isomers. A previous study,[6] in which η^4-coordinated butadienes were synthesised, supports our proposed *cis*–*trans* isomer mixture.

Based on the preceding observations, we propose the following mechanism for the double carbene insertion. The rate of reaction is very slow below 60 °C which indicates the initial dissociation of phosphine to form the 16e intermediate **A** (Scheme 1).[3,5,6] The α-diazo ketone coordinates to **A** which then undergoes carbene insertion *via* a possible cobalt–carbene intermediate **B**. The carbene is inserted into the metallocycle ring to form the intermediate **C**. In a previous study,[5] the cobaltacyclohexadiene intermediate had electron withdrawing ring substituents which reduced overlap in the cobalt–carbon bonds. This overlap had already been reduced by dissociation of the phosphine[3] and so reductive elimination took place to form an η^4-coordinated cyclopentadiene.

In our reactions, the methyl substituents on the ring in **C** inductively stabilize it so that it may react with another molecule of the diazo ketone. The coordination of the diazo

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† Silica gel at low temperature (dry-ice jacket) under nitrogen, eluting with hexane–diethyl ether.

‡ *Selected spectroscopic data for* **3a**, **b** and **c**: IR(KBr), ν_{co}/cm^{-1} **3a** 1674, 1653; **3b** 1716, 1668; **3c** 1695, 1664. Mass spectrometry, M^+, **3a** *m/z* 344; **3b** 372; **3c** 496. ^1H NMR, (300.13 MHz). *trans*-**3a** δ 4.52 (s, 5H, C_5H_5), 4.97 [s, 1H, H(8)], 0.23 [s, 1H, H(17)], 1.47 [s, 3H, $C(10)H_3$], 2.09 [s, 3H, $C(12)H_3$], 2.50 [s, 3H, $C(14)H_3$], 2.42 [s, 3H, $C(16)H_3$]. *cis*-**3a** δ 4.47 (s, 5*H*, C_5H_5), 5.57 [s, 1*H*, H(8)], 0.18 [s, 1H, H(17)], 1.44 [s, 3H, $C(10)H_3$], 1.55 [s, 3H, $C(12)H_3$], 2.09 [s, 3H, $C(14)H_3$], 1.82 [s, 3H, $C(16)H_3$]. **3b** (mixture) δ 4.49/4.45 (s, 5H, C_5H_5), 4.94/5.54 [s, 1H, H(8)], 0.25/0.21 [s, 1H, H(17)]. **3c** (mixture) δ 4.32/4.30 (s, 5H, C_5H_5), 5.43/4.84 [s, 1H, H(8)], −0.05/0.10 [s, 1H, H(17)].

§ *Crystal data* for **3a**: $C_{19}H_{25}O_2Co$, $M = 344.3$, triclinic, space group $P\bar{1}$, $a = 7.840(4)$, $b = 8.433(4)$, $c = 14.701(5)$ Å, $\alpha = 92.17(3)$, $\beta = 100.83(3)$, $\gamma = 116.41(4)°$; $U = 847.34(79)$ Å^3, $Z = 2$, $D_c = 1.35$ g cm^{-3}, Mo–Kα radiation, $R = 0.067$ for 3083 unique reflections with $I > 3\sigma$ collected in the range $6° \leq 2\theta \leq 60°$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ketone to **C** may take place from two sides leading to the R groups in the cobalt heptadienyl intermediate **D** being on either the same or opposite sides of the ring. In the reductive elimination of **D**, which is a concerted reaction, this may lead to a *cis* or *trans* arrangement about C(8)–C(9).¶ A study of a model of **D** indicates that reductive elimination leading to *cis*-conformations on the terminal double bonds is prohibited by steric repulsion between R substituents. A kinetic study on the insertion of alkynes into cobaltacyclopentene metallocycles[7] supports our proposal of the cobaltacycloheptadiene intermediate **D**.

The reaction of metallocycles with various reagents is an important route to the synthesis of highly substituted cyclic compounds. The insertion of carbenes is a new and relatively unexplored area of this type of chemistry. The results from this study contribute to a better understanding of reactions which have significant potential as synthetic tools.

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¶ The ratio *trans* : *cis* calculated from integrals of the ^{1}H NMR spectra are: **3a** 54 : 46, **3b** 34 : 66, **3c** 14 : 86%.