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Preliminary communication

Synthesis of μ-carbene complexes of cobalt from substituted diazirines *

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Abstract

Treatment of $[(\eta^5\text{-}C_5Me_5)_2Co_2(\mu\text{-}CO)_2]$ with aryl(methoxy)diazirines in dichloromethane affords the μ-carbene complexes $[(\eta^5\text{-}C_5Me_5)_2Co_2(\mu\text{-}CO)_2\{\mu\text{-}C(OMe)Ar\}]$ in high yield (Ar = $4\text{-}FC_6H_4$, $4\text{-}MeC_6H_4$). Characterisation by ^1H and ^{13}C NMR spectroscopy indicates a novel dynamic process with restriction of rotation about the C–Ar axis.

There is considerable interest in the synthesis of μ-carbene complexes [1] because of their significance in catalytic reactions, and as models for carbene species bonded to metal centres. We have recently reported a new route to the preparation of such species from diazirines, and have described the preparation and characterisation of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(CO)_2\{\mu\text{-}C(OMe)Ar\}]$ by carbene addition to $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2]$ [2]. We now describe the analogous reactions in the cobalt series, which show significant differences.

Dropwise addition of a pentane solution of an excess of an aryl(methoxy)diazirine (**1**) [3], to a rapidly stirred solution of $[(\eta^5\text{-}C_5Me_5)_2Co_2(\mu\text{-}CO)_2]$ [4] in dichloromethane at room temperature over 4–5 h resulted in a darkening of the green colour of the solution, and on evaporation of the solvent a dark green solid was obtained. Recrystallisation (EtOH, −78 °C, (**2a**); EtOH/CH_2Cl_2, −78 °C, (**2b**)) gave $[(\eta^5\text{-}C_5Me_5)_2Co_2(\mu\text{-}CO)_2\{\mu\text{-}C(OMe)Ar\}]$ (**2**) (**2a** 77%; **2b** 65%) as microcrystalline green solids.

A number of differences from the rhodium complexes (**3**), previously prepared by the same method, were noteworthy. Firstly, IR spectroscopic data (KBr) clearly indicated that the carbonyl groups in **2** were bridging (**2a** ν(CO) 1817, 1781 cm^{-1}; **2b** ν(CO) 1820, 1783 cm^{-1}) rather than terminal as in **3** (**3a** ν(CO) 1961, 1942

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* Dedicated to Professor Eaborn in honour of his 65th birthday.

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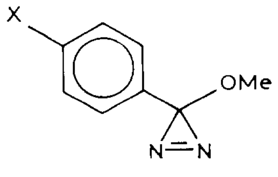
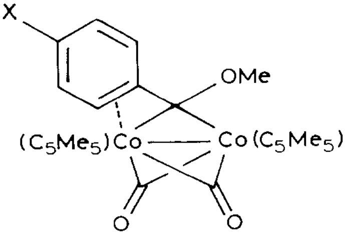


(**1a**, X = Me ;
1b, X = F)



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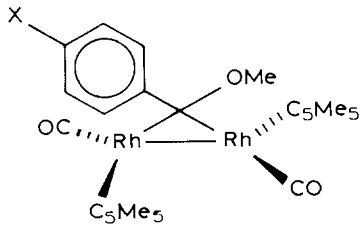

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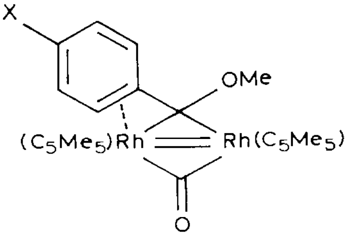

(**4a** , X = Me ;
4b , X = F)

cm^{-1}). Solution data (CH_2Cl_2) were similar, which precludes the possibility of an equilibrium between terminal and bridging forms for **2** in solution. The stretching frequencies were quite similar to those observed for well established dicobalt μ-carbene μ-dicarbonyl complexes [5,6]. Additionally, ^{13}C NMR spectroscopy gave resonances at δ 251.4 and 249.2 for the stereochemically distinct carbonyl groups (243 K) in **2a** and δ 252.0 and 250.4 for those in **2b**, these values being typical of bridging rather than terminal groups [6]. These signals were broadened at room temperature, and investigations into the dynamic process involved are underway. This result might be attributed to a greater degree of steric crowding in **2** than in **3** and a shorter metal–metal bond.

The corresponding rhodium complex (**3a**) was fully characterised by X-ray diffraction and was shown to possess terminal carbonyl ligands with no interaction between the aryl ring and either metal centre. However, in **4**, formed on thermolysis of **3**, rotation about the C–aryl bond was slow on the NMR timescale, and at low temperature the two "sides" of the aryl ring could be distinguished in both the ^1H and the ^{13}C NMR spectrum. Similar dynamic behaviour was noted in the NMR spectrum of **2**. For **2a** at 303 K, the proton NMR spectrum for the aryl region showed two signals at δ 7.27 (broad, 2H), assigned to H(2) and H(6), and δ 6.99 (^3J(HH) 7.9 Hz, 2H), assigned to H(3) and H(5). At 223 K, however, the signal at δ 7.27 was split into two signals centred at δ 7.45 (d, ^3J(HH) 7.4 Hz, 1H) and δ 6.97 (broad, 3H). Comparison with the data for the rhodium complex suggests that the resonance at δ 7.45 should be assigned to H(6) and that at δ 6.97 to H(2), H(3), and

H(5). ^{13}C NMR spectroscopy gave analogous results (303 K, δ 127.4, C(3)C(5), signal for C(2)C(6) very broad; 243 K, δ 130.7 C(6), 128.2 C(5), 126.8 C(3), 120.8 C(2)). Comparable data were obtained from **2b** (^{1}H NMR spectrum *, 293 K, δ 7.40 (broad, 2H, H(2), H(6)) 6.88 (t, 2H, H(3), H(5), $^3J(\mathrm{HH}) \approx {}^3J(\mathrm{HF})$ 8.6 Hz); 253 K, δ 7.78 (m, 1H, H(6)), 7.14 (m, 1H, H(2)), 6.88 (broad, 2H, H(3), H(5)); ^{13}C NMR spectrum, 308 K, δ 114.4 (C(3), C(5)), signal from C(2) and C(6) too broad for observation; 233 K, δ 133.3 (d, ^3J(CF) 7 Hz, C(6)), 123.6 (d, ^3J(CF) 7 Hz, C(2)), 115.4 (d, ^2J(CF) 21 Hz, C(5), 113.7 (d, ^2J(CF) 21 Hz, C(3))). We conclude that rotation about the C–aryl bond is restricted in **2**, due to a weak interaction between the aryl ring and one of the cobalt atoms. There have been a number of precedents for such interactions [8,9] but final confirmation awaits a crystal structural determination.

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* Aromatic regions of the spectra only given.