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Cobalt isocyanide complexes

Ian Beaumont and Anthony H. Wright
Chemistry Department, University of Nottingham, Nottingham NG7 2RD (UK)

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Abstract

The synthesis and properties of mono and bis-isocyanide complexes of cobalt(I), CpCoLL′, are described, together with migration reactions involving the isocyanide and the cyclopentadienyl ligand.

The wide variety of complexes of the type $CpML_2$, where M = Co, Rh and Ir, include several reports where L = isocyanide [1]. Recent attention has focused on rhodium [2], but even so little attention has been paid to the reactivity of the complexes.

This paper is part of a study of the reactions of the CpCo unit with groups containing a CN multiple bond [3] and focuses on $CpCo(CNR)_2$ complexes. A general synthesis is described and a number of reactions discussed. These reactions point to much more diverse chemistry than is seen for the carbonyl analogues.

When $CpCo(C_2H_4)_2$ [4] is treated with isocyanide (p-tolyl or tert-butyl) at low temperature a single ethylene ligand is substituted and solid $CpCO(CNR)(C_2H_4)$ (**1**, R = ^{t}Bu), (**2**, R = *p*-tolyl), may be isolated (Scheme 1). These complexes are however thermally unstable and readily react with further isocyanide at ambient temperatures to give the bisisocyanide complexes **3** and **4**.

The products are an orange liquid (**3**, R = ^{t}Bu) or low-melting brown solid (**4**, R = *p*-tolyl) and NMR spectra are entirely as expected. However solution IR spectra show 3 or 4 bands in the ν(CN) region. This is a phenomenon that has been recently reported in the related rhodium system, without explanation [5].

Two possible causes for this existence of multiple bands are being examined. Since $Cp^{\star}Co(CO)_2$ has been shown to exist in a prefered conformation in the solid state [6] there is the possibility that there are two, distinct, thermally accessible conformations due to the cyclopentadienyl ligand. Alternatively the multiple bands may arise from bending of the isocyanide ligands giving rise to different conform-

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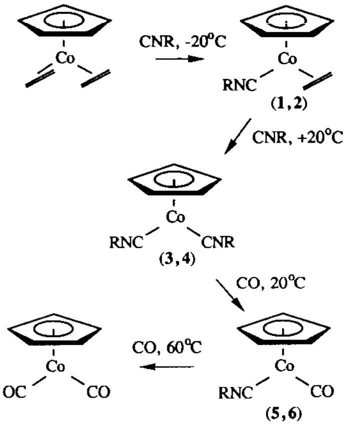
Correspondence to: Dr. A.H. Wright, Chemistry Department, University of Nottingham, Nottingham NG7 2RD, UK.

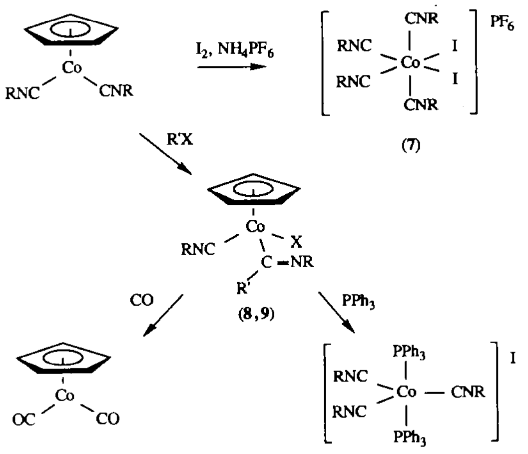


Scheme 1

ers in solution. A study of the solution and solid state structures of a related chromium complex has suggested that ligand bending is the cause of the multiple bands [7]. A preliminary study of variable temperature IR spectra indicates that two chemically different species exist in solution, but it is not possible to distinguish between the two possible causes [8].

The character of the Co–isocyanide bond appears to be intermediate between Co–ethylene and Co–carbon monoxide based on the facile substitution of ethylene by isocyanide and isocyanide by CO. Thus when treated with CO, **3** and **4** undergo monoisocyanide substitution to give the complexes CpCo(CNR)(CO) (**5**, **6**). Mild heating of the reaction mixture leads to further substitution and the dicarbonyl complex, $CpCo(CO)_2$, is formed.

As well as undergoing facile nucleophilic substitution reactions, the complexes **3** and **4** can also be regarded as metal bases [9], reacting rapidly with oxidants and electrophilic reagents (Scheme 2). The reaction of **3** with iodine is very rapid and a dark brown solid is readily isolated [10]. The ^{1}H NMR spectrum demonstrates that



Scheme 2

this material is a mixture of the cobaltocenium cation and a new compound that does not contain the cyclopentadienyl ligand. Metathesis of the anion with $[PF_6]^-$ has allowed characterisation of the product as $[CoI_2(CN^tBu)_4]PF_6$ (**7**).

The ability of the isocyanide ligand to participate in migration reactions is demonstrated in the reaction with alkyl halides, for which the most reasonable mechanism for the formation of the products **8** and **9** is a sequence of alkyl addition at cobalt followed by migration to carbon and subsequent halide addition to give the product.

This product is highly reactive towards nucleophiles but the products are unexpected. In the case of reaction with CO, reductive elimination occurs, and $CpCo(CO)_2$ is generated. However when **8** or **9** is treated with PPh_3 it is the cyclopentadienyl and not the isocyanide ligand that is displaced. The product [10] is readily characterised and the substituted cyclopentadienes can be identified from the mass spectra of the reaction mixtures.

The products can be understood in terms of haptotropic shifts of the cyclopentadienyl ring [11] being accompanied by migrations of the alkyl group to the metal. Subsequent reductive elimination of the alkyl and cyclopentadienyl groups would lead to the observed products. Whether or not such a reaction sequence is preceeded by loss of the iodide ligand has not been established. The iodide in **8** is highly labile, and can be trapped as AgI, although the resulting cobalt complex is not readily identified.

Characterisation data for complexes 1–9

1: $CpCo(C_2H_4)(CN^tBu)$. IR (Et_2O): ν(CN) 2060 cm^{-1}. ^1H NMR (C_6D_6): 4.69 (s, 5H, C_5H_5), 2.65 (m, 2H, C_2H_4), 1.99 (m, 2H, C_2H_4), 0.82 (s, 9H, $C(CH_3)_3$).

2: $CpCo(C_2H_4)(CN$-*p*-tolyl). IR (Et_2O): ν(CN) 2071, 2042 cm^{-1}. MS (EI) *m/z*: 241 ($M^+ - C_2H_4$).

3: $CpCo(CN^tBu)_2$. IR (hexane): ν(CN) 2090 sh, 2052, 1933 cm^{-1}. ^{1} H NMR (C_6D_6): 4.94 (s, 5H, C_5H_5), 1.12 (s, 18H, $C(CH_3)_3$). MS (EI) *m/z*: 207 ($M^+ - CN^tBu$). Anal. Found: C, 61.65; H, 7.95; N, 9.25. $C_{15}H_{23}CoN_2$ calc.: C, 62.05; H, 8.00; N, 9.65%.

4: $CpCo(CN$-*p*-tolyl$)_2$. IR (pentane): ν(CN) 2085, 2055, 1995, 1959 cm^{-1}. ^1H NMR (C_6D_6): 7.00–6.58 (m, 8H, C_6H_4), 5.02 (s, 5H, C_5H_5), 1.88 (s, 6H, CH_3).

5: $CpCo(CO)(CN^tBu)$. IR (Et_2O): ν(CN) 2112, 2071, ν(CO) 1937 cm^{-1}. ^1H NMR (C_6D_6): 4.75 (s, 5H, C_5H_5), 0.91 (s, 9H, $C(CH_3)_3$), MS (EI) *m/z*: 235 (M^+).

6: $CpCo(CO)(CN$-*p*-tolyl). IR (Et_2O): ν(CN) 2095, 2045, ν(CO) 1946 cm^{-1}. ^1H NMR (C_6D_6): 6.90–6.31 (m, 4H, C_6H_4), 4.79 (s, 5H, C_5H_5), 1.83 (s, 3H, CH_3).

7: $[CoI_2(CN^tBu)_4]PF_6$. IR (CH_2Cl_2): ν(CN) 2190, 2160 cm^{-1}. ^1H NMR ($CDCl_3$): 1.6, 1.5 (s, 36H, $C(CH_3)_3$). MS (EI) *m/z*: 895 (M^+).

8: $CpCoI(CMeN^tBu)(CN^tBu)$. IR (CH_2Cl_2): ν(CN) 2169, 1818 cm^{-1}. ^1H NMR ($CDCl_3$): 5.23 (s, 5H, C_5H_5), 3.28 (s, 3H, CH_3), 1.38, 1.37 (s, 18H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): 157, 139.4 (*C*N^tBu), 85.7 (Cp), 60.4, 59.1, (*C*$(CH_3)_3$), 31.6, 30.0 ($C(\mathit{C}H_3)_3$), 20.1 (CH_3). MS (EI) *m/z*: 432 (M^+). Anal. Found: C, 44.53; H, 5.80; N, 6.85. $C_{16}H_{26}CoIN_2$ calc.: C, 44.45; H, 6.07; N, 6.48%.

9: $CpCoBr(C(CH_2C_6H_5)N^tBu)(CN^tBu)$. IR ($CH_2Cl_2$): ν(CN) 2182, 1805 cm^{-1}. ^1H NMR (C_6D_6): 7.07–6.91 (m, 4H, C_6H_5), 3.20 (s, 2H, CH_2), 4.30 (s, 5H, C_5H_5), 1.22, 1.16 (s, 18H, $C(CH_3)_3$). MS (IE) *m/z*: 461 (M^+).

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