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Synthesis and Reactivity of Cobalt Complexes with Pendant Nitrogen Functional Groups

Longjin Li,[a] Shuang Han,[b] Qiang Li,[a] Zhenxia Chen,[a] and Zhen Pang*[a]

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Several derivatives of cyclopentadienylcobalt complexes having a pendant amino-functionalised side chain (Cp′) are described, the cyclopentadienyl ligands being (2-aminoethyl)cyclopentadienyl, (2-piperidinoethyl)cyclopentadienyl, 1-(2-piperidinoethyl)-2,3,4,5-tetraisopropylcyclopentadienyl and 2-picolylcyclopentadienyl. Chelation by the amino-functionalised side chain occurred when the Cp*-cobalt(I) dicarbonyl complexes **5**, **6**, **7** and **8** were oxidised by iodine, thereby forming the corresponding Cp*-cobalt(III) chelates **9**, **10**, **11** and **12**, respectively, through the diiodocarbonyl intermediates **5**′, **6**′, **7**′ and **8**′, respectively. The stabilities of the intermediates differ greatly due to the different amino functions in the pendant side chain. Structural studies of **9**, **10** and **12** were carried out and the correlation of the I–Co–I angles and the repulsive forces from the amino-functionalised groups with the stabilities of the intermediates is discussed. The diiodocarbonyl-η^5-(2-piperidinylethyl)cyclopentadienylcobalt(III) intermediate **6**′ becomes reduced to **6** by the CO released upon chelation of the former when the concentration of CO reaches about 0.088 mol L^{-1}. The chelated piperidine group in **10** could be easily replaced by triphenylphosphane to form the diiodotriphenylphosphanyl-η^5-(2-piperidinioethyl)cyclopentadienylcobalt(III) iodide dichloromethane solvate **13** in the presence of hydrogen iodide. A strong N–H···I hydrogen bond with an N···I distance of 3.414(14) Å and a D–H···A angle of 164.1° were found in **13**.

Introduction

The cyclopentadienyl group is one of the most important ligands in organometallic chemistry.[1] Its derivatives with Lewis bases in a pendant side chain that are capable of binding to hard and soft centres in a hemilabile manner promise a rich coordination chemistry and unusual reactions at the metal centre.[2] The Lewis bases may included alkenes,[3] phosphorus atoms,[4] thioethers, ethers and ester groups.[5] N-Based Lewis bases tethered to the Cp ligand have been frequently used as hemilabile ligands. Such ligands can only weakly coordinate to late transition metal centres forming a chelate bond which can also be easily broken under mild conditions. Since the binding strength between the metal and the donor ligand can be controlled sterically or electronically, structural modification to such a pendant side chain can greatly influence the physical and chemical properties of these complexes[6] and some molecular switches, which have been designed, are based on this concept.[7,8] Furthermore, the weak coordinate bond in these complexes can be easily broken under mild condition thereby creating a vacant site on the metal and such complexes therefore have applications in catalysis. The reactivity of the active intermediate is strongly influenced by the changes in the electronic density on the metal centre and the steric nature of the chelating donor moiety. Thus, an improved understanding of the factors governing the chelation of the tethered functional group should lead to more control over the design of more efficient catalytic processes. Many complexes with a chelating pendant Lewis base tethered to a Cp ligand have be synthesised and studied.[9–22] We are interested in the chemistry of the half-sandwich type complexes with a pendant chelating functional group, especially those containing nitrogen atoms in the pendant side chain and in the factors which can influence the ability of the pendant group to chelate to the metal. In this paper we report the synthesis and reactivity of several cobalt complexes with nitrogen functionalised pendant side chain cyclopentadienyl ligands.

Results and Discussion

Four compounds $C_5H_5CH_2CH_2NH_2$ (**1**), $C_5H_5CH_2CH_2NC_5H_{10}$ (**2**), $C_5(C_3H_7)_4HCH_2CH_2NC_5H_{10}$ (**3**) and $C_5H_5CH_2NC_5H_4$ (**4**) with a space of two carbon atoms between the nitrogen atom and cyclopentadienyl ring were all synthesized using a similar strategy, i.e. treatment of so-

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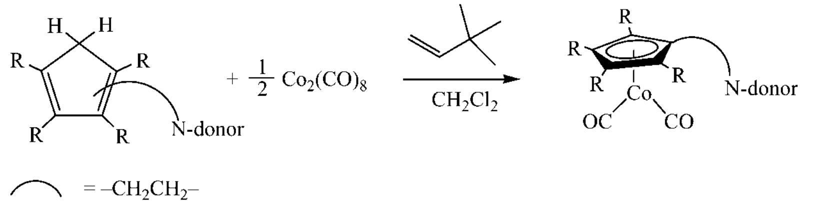
[a] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials,
Fudan University, Shanghai 200433, P. R. China
E-mail: zpang@fudan.edu.cn
[b] Department of Chemistry, Yuncheng College of Shanxi Province,
Yuncheng City, Shanxi Province 044000, P. R. China



1, R = H, N-donor = -NH_2
2, R = H, N-donor = cyclo-NC_5H_{10}
3, R = -$CH(CH_3)_2$, N-donor = *cyclo*-NC_5H_{10}
4, R = H, N-donor = NC_5H_4

5, R = H, N-donor = -NH_2
6, R = H, N-donor = cyclo-NC_5H_{10}
7, R = -$CH(CH_3)_2$, N-donor = *cyclo*-NC_5H_{10}
8, R = H, N-donor = NC_5H_4

Scheme 1.

dium cyclopentadienide with a suitable halogenated alkylamine followed by standard aqueous workup. Because of the good solubility of **1** in aqueous solution, strong acidic ($pH < 1$) and basic ($pH > 14$) conditions must be kept during the aqueous workup in order to increase the yield. The reaction of compounds **1**–**4** with $Co_2(CO)_8$ in dichloromethane in the presence of a sacrificial olefin 3,3-dimethyl-1-butene gave the substituted dicarbonylcyclopentadienylcobalt(I) complexes **5**–**8** in moderate yields, Scheme 1.[23] If the syntheses were to be done in a higher boiling point solvent, the yields should increase.

All the dicarbonylcobalt(I) complexes show two characteristic absorption bands in their IR spectra indicating that two terminal carbonyl groups are present and that the nitrogen atoms in the side chains do not coordinate to the cobalt atoms. No chelation was observed between the cobalt(I) and the nitrogen functional group except under irradiation of light.[24] The characteristic ν(CO) data are listed in Table 1.

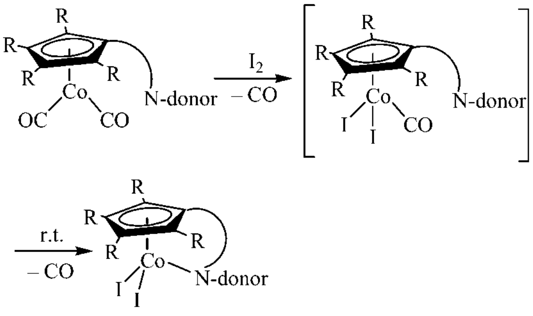
Table 1. Characteristic CO stretching frequencies of dicarbonylcobalt(I) complex and their corresponding diiodo-monocarbonylcobalt(III) intermediates.

$Cp'(CO)_2Co$	ν(CO) [cm^{-1}][a]	Monocarbonyl	ν(CO) [cm^{-1}]
5	2017, 1951	**5′**	2068[b], 2074[c]
6	2019, 1954	**6′**	2060[b], 2066[c]
7	2003, 1943	**7′**	2050[a], 2046[b]
8	2016, 1948	**8′**	2077[c]

[a] Neat sample. [b] KBr pellets. [c] Dichloromethane solution.

Complexes **5**–**8** can be easily oxidised by iodine to yield the corresponding cobalt(III) complexes.[25] It has been reported that when iodine is added to an ether solution of carbonyl cyclopentadienylcobalt(I) complexes with an N-donor function in the side chain, the corresponding chelated diiodo-cobalt(III) complexes precipitate spontaneously from the reaction mixture as black microcrystals.[24a] It is believed that the chelate is formed via the diiodocarbonyl complex (vide infra) since, when the CO-free chelate precipitates, the solution is still dark purple in colour indicating the presence of the monocarbonyl species and this is supported by ^1H NMR spectroscopic observations. In our experiment, the observations made upon the addition of iodine to the dichloromethane solutions of **5**–**8** are consistent with the literature report because they show evidence of the appearance of a strong carbonyl absorption band at higher frequencies for the solutions which is in contrast to the two carbonyl stretching frequencies observed for the precursors. This carbonyl absorption must come from the reaction intermediates **5′**–**8′** as listed in Table 1. However, in all cases, the black purple precipitate appeared immediately after the addition of iodine and the isolated precipitates also showed one carbonyl absorption band. Elemental analyses and ^1H NMR spectroscopy indicated that the isolated products were mixtures of the CO-free chelates **9**–**12** and their corresponding diiodocarbonyl complexes **5′**–**8′**. For example, the ^1H NMR spectrum of the precipitate obtained from the solution of iodine and **5** shows three peaks at δ = 4.22, 3.60 and 2.42 ppm. The first and third peaks result from the methylene groups between the cyclopentadienyl and amino groups in chelate **9**. The peak of 3.60 ppm could also come from the dimethylene group but it is shifted 0.12 ppm downfield compared with the similar resonance in **5**, indicating a free side chain in the Co^{III} product **5′**. A carbonyl stretching frequency at 2068 cm^{-1} was found for the solid but its intensity diminished at room temperature after one weak indicating the existence of the unstable **5′** and, hence, the isolated solid was initially a mixture of **5′** and **9**. The carbonyl stretching frequency of the solid product isolated from a solution of iodine and **6** or **7** was found at 2060 or 2046 cm^{-1}, respectively, but the signal disappeared at room temperature after about one day indicating the isolated products to be mixtures of **6′** and **10** or **7′** and **11**, respectively. Only the precipitate isolated form a solution of iodine and **8** gave the pure chelated product **12**. The stability of the reaction intermediates is therefore of the order **5′** > **6′**:**7′** > **8′**. The oxidising process is illustrated in Scheme 2.

The crystal structures of the chelates **9**, **10** and **12** were determined and all of them show that the tethered amino group is intramolecularly coordinated to the cobalt atom. The ORTEP diagrams and the selected structural parameters of **9**, **10** and **12** are given in Figure 1, Figure 2 and Figure 3. The Co–N bond lengths in **9**, **10** and **12** were found to be 1.979(8), 2.097(3) and 1.956(6) Å, respectively. All of these bond lengths are slightly shorter than those in related tetramethyl-substituted diiodocyclopentadienylcobalt(III) complexes, e.g. 2.115(6) Å in diiodo-η^5:η^1-[l-(2-*N*,*N*-dimethylaminoethyl)-2,3,4,5-tetramethyl cyclopenta-



9, N-donor = $-NH_2$, R = H
10, N-donor = *cyclo*-NC_5H_{10}, R = H
11, N-donor = *cyclo*-NC_5H_{10}, R = $-CH(CH_3)_2$
12, N-donor = NC_5H_4, R = H

Scheme 2.

dienyl] cobalt(III) ("aminoethyl")[24a] and 2.205(2) Å in diiodo-η^5:η^1-[l-[2-(dimethylamino)phenyl]-2,3,4,5-tetramethylcyclopentadienyl]cobalt(III) ("aminophenyl").[18] Considering that the alkyl ring of piperidine is an electron-releasing substituent, the nitrogen atom in the tethered side chain in **10** should be a stronger σ donor compared with that in **9** and **12** and the chelate bond in **10** would be expected to be the strongest one among the three analogues. However, the chelate bond in **10** was found to be the longest. For easy comparison between these analogues, some structural parameters are listed in Table 2. The average lengths of the Co–I bonds in **9**, **10** and **12** are 2.5979(10), 2.5865(3) and 2.5788(16) Å, respectively − all slightly shorter than 2.622(2) Å found in "aminoethyl" and 2.604(1) Å found in "aminophenyl". The average cobalt–carbon(ring) bond lengths show the same trend but all are still in the expected range. The I–Co–I bond angles are 96.50(5), 92.70(2) and 96.68(4) degrees in **9**, **10** and **12**, respectively. The corresponding values reported for "aminoethyl" and "aminophenyl" are 94.5(1) and 91.302(12)°, respectively. The I–Co–N bond angles found in **9**, **10** and **12** are 92.07(16), 100.32(8) and 95.12(18)°, respectively. A comparison of the above structural data indicates that a large repulsive force might exist in **10** between the iodine ligands and the methylene groups in the piperidine ring adjacent to the nitrogen atom which pushes the iodine ligands away from the piperidine moiety and leads to the smallest I–Co–I angle as well as the longest Co–N bond length among the three chelates.

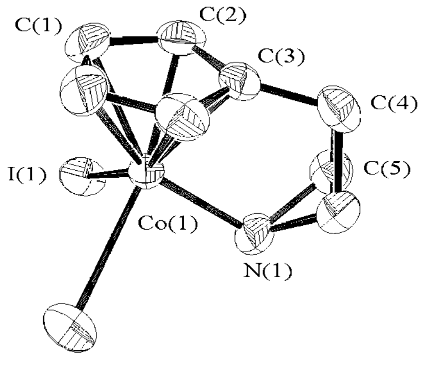


Figure 1. ORTEP diagram of **9** with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Average Co–C(ring) 2.045(1), Co(1)–N(1) 1.979(8), Co(1)–I(1) 2.5979(10), Average C–C(ring) 1.4054(4), I(1)–Co(1)–I(1A) 1 96.50(5), I(1)–Co(1)–N(1) 92.07(16), I(1A)–Co(1)–N(1) 92.07(16), Co(1)–N(1)–C(5) 110.3(7).

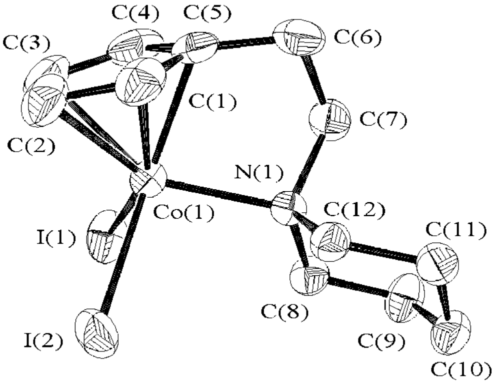


Figure 2. ORTEP diagram of **10** with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Average Co–C(ring) 2.055(6), Co(1)–N(1) 2.097(3), Co(1)–I(1) 2.6015(7), Co(1)–I(2) 2.5714(8), average C–C(ring) 1.4084(6), I(1)–Co(1)–I(2) 92.70(2), I(1)–Co(1)–N(1) 100.32(8), I(2)–Co(1)–N(1) 96.34(9), Co(1)–N(1)–C(7) 104.1(2).

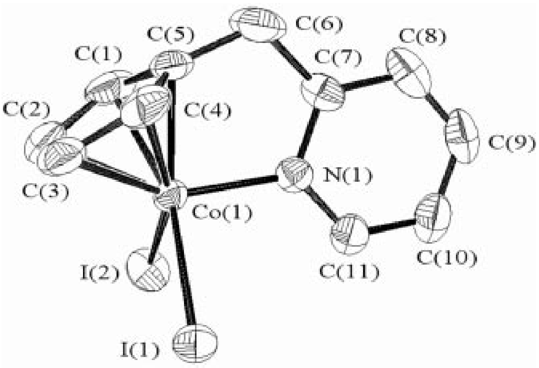


Figure 3. ORTEP diagram of **12** with the probability ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Average Co–C(ring) 2.039(8), Co(1)–N(1) 1.956(6), Co(1)–I(1) 2.5779(16), Co(1)–I(2) 2.5796(16), average C–C(ring) 1.403(14), N(1)–C(7) 1.351(10), N(1)–C(11) 1.327(10), C(7)–C(8) 1.392(12), C(8)–C(9) 1.360(14), C(9)–C(10) 1.370(14), C(10)–C(11) 1.365(12), I(1)–Co(1)–I(2) 96.68(4), I(1)–Co(1)–N(1) 95.12(18), I(2)–Co(1)–N(1) 95.12(19), Co(1)–N(1)–C(7) 116.9(5).

The COSY spectrum of **10** reveals that the methylene protons in the piperidine ring adjacent to nitrogen atom suffer large steric hindrance and retain their configuration in solution at room temperature (Figure 4). The methylene protons on the α carbon in the piperidine ring are split into two sets of signals. The signals of the protons in the *e* position at $\delta = 3.52$ show a strong correlation with the methylene protons on the β carbon in the piperidine ring ($\delta = 1.72$ ppm) and the signals of the protons in the *a* position at $\delta = 2.93$ show a strong correlation with the methylene

Table 2. List of the structural parameters of the cyclopentadienylcobalt complexes with a nitrogen functional group in the pendant side chain.

Chelates	I–Co–I [°]	Co–N [Å]	Co–I_{av} [Å]	Co–$C(ring)_{av}$ [Å]
9	96.50(5)	1.979(8)	2.5979(10)	2.044(7)
10	92.70(2)	2.097(3)	2.5865(3)	2.055(4)
12	96.68(4)	1.956(6)	2.5788(16)	2.039(8)
13	95.40(8)	2.239(5) (Co–P)	2.580(3)	2.094(17)
Aminoethyl[24a]	94.5(1)	2.115(6)	2.622(2)	2.095(5)
Aminophenyl[15]	91.302(12)	2.205(2)	2.604(1)	2.080(3)

protons on the ω carbon in the piperidine ring (δ = 1.22 ppm). The methylene protons on the β carbon in the piperidine are in a free-flipping motion and give rise to a broadened multiplet. We can deduce that the flipping of the methylene protons on the α carbon in the piperidine ring in **10** is prevented by steric hindrance in the chelated form. This steric hindrance results from the repulsive force of the iodine ligands which keeps the σ orbitals between cobalt and the amino nitrogen from fully overlapping and thus a longer chelate Co–N bond results. The side chains in **9** and **10** are coordinated to the cobalt in a zigzag fashion and, consequently, the latter can be expected to exist as chiral molecules. However, the very fast flip of the side chain makes the two enantiomers show only one set of signals in their ^{1}H NMR spectra. Similar situations have also been found in "aminoethyl" and "aminophenyl" and by Wang et al. in the molybdenum complex $[C_5H_4CH_2CH_2NMe_2]$-$Mo(CO)_2I$.[26] In the crystal structure of **12**, an idealised mirror plane of the Cp^*CoI_2 fragment was found which almost coincides with the plane of the pyridine ring. The observed orientation allows the maximum overlap between the π system in pyridine and one of the two suitable d-type donor orbitals at the cobalt centre.[27] Pyridine is considered a moderate π acceptor because its LUMO is not as low in energy as, for example, that of pyrazine which is known as a good π acceptor.[28] Thus, besides the normal σ interaction, a weak π interaction between the metal and donor nitrogen is also possible. This binding pattern between the nitrogen and cobalt results in the shortest Co–N bond among the three. In the indenyl-nickel analogues reported by L. E. Groux and D. Zargarian,[30] N–C bond lengths and C–C bond lengths in the tethered pyridine moiety were found to be longer in the chelated form [average 1.354(3) Å and 1.376(3) Å, respectively] than in the non-chelated form [average 1.335(5) Å and 1.360(6) Å, respectively]. Thus a delocalisation of electron density from nickel to the pyridine π system could be assumed. The corresponding N–C bond lengths [average 1.339(10) Å] and the C–C bond lengths [average 1.372(13) Å] found in **12** are comparable with those of the chelated forms of the indenyl-nickel complexes. Comparing the slightly shorter C–C bond lengths in the Cp ring [average 1.403(14) Å] found in **12** with the corresponding data for **9** and **10** [average 1.4054(4) and 1.4084(6) Å, respectively], a possible delocalisation of electron density from cobalt to the pyridine π system is likely. The σ, π interaction between a donor atom possessing d orbitals (such as S and P from the ligand) and the metal in half-sandwich complexes is also known.[31,32] Although nitrogen does not have an available d orbital, the π system of pyridine makes the donor nitrogen atom in the tethered side chain of **12** undergo a stronger interaction with the metal compared with an S or P atom. Thus we may assert that there is a partial double bond in existence in **12** which leads to a shorter Co–N bond.

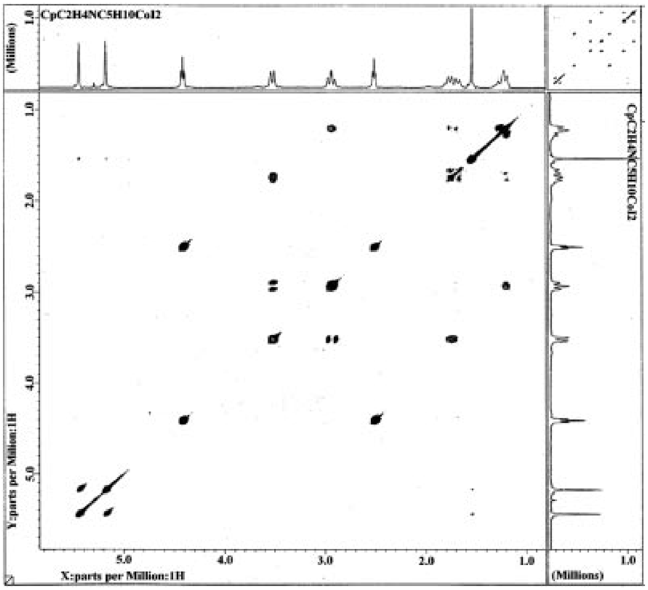


Figure 4. COSY spectrum of diiodo-η^5:η^1-(2-piperidinoethyl)cyclopentadienylcobalt(III) ($C_5H_4C_2H_4N_5H_{10}CoI_2$) (**10**) in $CDCl_3$ at 25 °C.

Since the metal–CO bond is weaker[25] for the cobalt(III) complex compared with that in the cobalt(I) complex, the amino nitrogen as a σ donor in the pendant side chain can replace the CO group in the oxidised diiodocarbonyl intermediates. Although there is greater steric hindrance around the donor atom in the piperidine moiety compared with the amino moiety, the formation of **10** was still found to be much faster than that of **9**. This phenomenon suggests that the rate of chelation might be determined by the strength of the Lewis basicity of the nitrogen atom in the donor function. However, by oxidation of **8** with iodine, pure **12** was obtained directly and we did not find a carbonyl adsorption band in the precipitate thus indicating the chelation here is the fastest among the four dicarbonyl reaction precursors. If the σ donor ability of the lone pair on the nitrogen atom in the pendant side chain were only determined by the hybridisation of the orbital, the rate of chelation in **8** should be slower than was observed in **6** or **7**. The driving force for the faster rate of chelation can be attributed to the formation of a partial double bond between cobalt and nitrogen. The π interaction between cobalt(III) and nitrogen as well as the less steric hindrance and the low degree of freedom in the functionalised arm in **8** are more than enough to compensate for the lower σ donor ability of the N-based pendant function. Thus, the shortest lifetime of the diiodocarbonyl intermediate **8′** and the fastest rate of chelation observed during the oxidation process of **8** can be understood.

It has been demonstrated by Jutzi et al. that performing the reduction of diiodo cobalt(III) chelates with sodium amalgam under an atmosphere of carbon monoxide leads to the formation of dicarbonylcobalt(I) species. Without the presence of sodium amalgam, only diiodocarbonylcobalt(III) was formed in an equilibrium with the corresponding diiodo cobalt(III) chelate.[24,29] Irreversible displacement of the intramolecular coordinated ligand was only achieved under very drastic conditions. In our experiments, we found that carbon monoxide not only replaced the intramolecularly coordinated ligand but also reduced the cobalt(III) complex to a cobalt(I) complex. In a airtight reaction vessel, we observed that the reaction intermediate diiodocarbonyl-η^5-(2-piperidinylethyl)cyclopentadienylcobalt(III) **6′** was reduced to its corresponding dicarbonylcobalt(I) **6** by the CO released during the chelation of the tethered piperidinyl ligand as shown by the IR spectrum depicted in Figure 5. Since the decay of the adsorption of the metal–carbonyl bond at 2066 cm^{-1} clearly shows the pattern of a first-order reaction and the plot of logA(ν_{CO}) vs. t has a good linear relationship ($R_2 > 0.999$) after an 882 s inducing period, the relationship between the concentration of the intermediate and time can be deduced. We estimated the initial absorbance ($t = 0$) of the diiodocarbonylcobalt(III) intermediate from the interception of the line with the ordinate by extrapolation. The carbonyl absorbance of **6** in dichloromethane was found obey the Lambert–Beer law quiet well within our experimental range. The concentration of each species at anytime can thus be calculated and such data are listed in Table 3. The reaction occurring in the IR cell can be described as shown in Scheme 3.

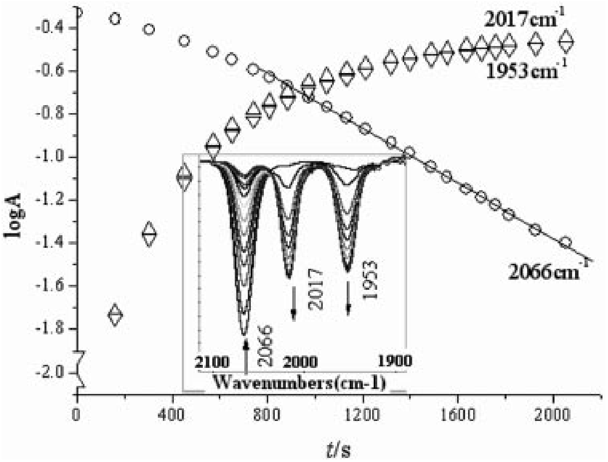
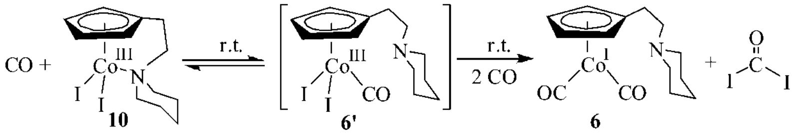


Figure 5. Reduction of diiodocarbonyl-η^5-(2-piperidinylethyl)cyclopentadienylcobalt(III) by carbon monoxide released via its own chelation. The inset IR spectra show the reducing ν(CO) of **6′** at 2066 cm^{-1} and the increasing ν(CO) of **6** at 2017 and 1953 cm^{-1}, respectively.

Table 3. Changes of the carbonyl absorbance during the chelation of **6** after being oxidised by iodine in dichloromethane solution.

	2066 cm^{-1}	2017 cm^{-1}	1953 cm^{-1}	CO released	CO consumed	free CO
t / s	A	A	A	[mol L^{-1}]	[mol L^{-1}]	[mol L^{-1}]
0	0.468	0.009	0.012			
161	0.439	0.019	0.018	0.174	0.0002	0.1674
304	0.391	0.046	0.042	0.188	0.0021	0.1659
451	0.346	0.086	0.076	0.202	0.0073	0.1574
571	0.309	0.119	0.107	0.214	0.0149	0.1502
651	0.283	0.142	0.128	0.222	0.0213	0.1448
742	0.255	0.166	0.149	0.23	0.0256	0.1396
808	0.235	0.183	0.165	0.236	0.0302	0.136
882	0.214	0.202	0.181	0.199	0.0335	0.0878
972	0.19	0.225	0.203	0.212	0.0371	0.0877
1050	0.171	0.24	0.217	0.222	0.0415	0.0892
1133	0.152	0.257	0.233	0.232	0.0444	0.0891
1213	0.135	0.271	0.249	0.24	0.0476	0.0893
1319	0.116	0.29	0.264	0.25	0.0503	0.088
1397	0.104	0.302	0.276	0.256	0.0539	0.0873
1487	0.09	0.313	0.287	0.262	0.0562	0.0873
1554	0.081	0.318	0.295	0.267	0.0583	0.0887
1634	0.071	0.33	0.301	0.271	0.0593	0.0863
1699	0.065	0.335	0.308	0.274	0.0616	0.0868
1757	0.06	0.342	0.313	0.277	0.0625	0.0855
1817	0.054	0.344	0.317	0.28	0.0639	0.087
1927	0.046	0.351	0.324	0.284	0.0643	0.0872
2052	0.04	0.359	0.331	0.288	0.0656	0.0867
					Average:	0.0876



Scheme 3.

According to Scheme 3, each molecule of the diiodocarbonyl intermediate **6′** can provide one molecule of carbon monoxide after chelation. To produce each molecule of dicarbonylcobalt(I) **6** requires three molecules of carbon monoxide. The difference between the consumed molecules of diiodocarbonyl intermediate **6′** and the formed molecules of **6** is the free carbon monoxide that dissolves in solution as listed in Table 3. Based on these data, our calculations reveal that after the first 882 s induction period, the difference in the concentration of the cobalt(III) and (I) species determined by IR measurements at the same time remains a constant 0.088 mol L^{-1}. Since the solubility of carbon monoxide in organic solvents cannot reach such a high lever under normal conditions, bubbling carbon monoxide through a solution of a cobalt(III) chelate cannot produce an oxidation state +1. We did not observe such self-reduction in similar experiments with **5** and **8**. This can be attributed to the rate of chelation in **9** being too slow to allow a sufficiently high concentration of carbon monoxide to form in the reaction vessel and also because a small leakage of CO from the IR cell cannot be entirely prevented. On the other hand, the rate of chelation in **12** is too fast and the carbon monoxide had already escaped form the reaction solution after the iodine had been added.

It is interesting to compare the properties of the tethered functional side chains in "aminoethyl", **10** and "aminophenyl" since the stereochemical environments around the Co–N bonds are similar. The diiodomonocarbonyl precursor of "aminoethyl" reported could only exist in solution under an atmosphere of carbon monoxide whereas the diiodomonocarbonyl analogue of **10** could be isolated in the solid-state but could not be fully characterised because of its instability; completion of the chelation was observed after only about one day. The diiodomonocarbonyl analogue of "aminophenyl" was isolated from a solution after 16 h stirring at room temperature under N_2 and in a yield of 58%. The big difference in chelating ability is consistent with the repulsive force between the iodine ligands and the methyl (methylene) groups adjacent to the nitrogen atom. A comparison of the structural parameters of these analogues using the values of I–Co–I bond angles and the Co–N bond lengths found the largest in "aminoethyl" and the smallest in "aminophenyl".

Triphenylphosphane is known to be a better ligand for late transition metal complexes than amines. At room temperature, triphenylphosphane can replace the intramolecularly coordinated piperidine group in **10**. Since triphenylphosphane is easily oxidised by iodine to form I_2PPh_3 which is itself readily hydrolysed by moisture to generate hydrogen iodide and triphenylphosphane oxide, the formed diiodotriphenylphosphanyl-η^5-(2-piperidinoethyl)cyclopentadienylcobalt(III) was thus protonated by hydrogen iodide to give the corresponding piperidinium salt **13**, crystals of which could be easily grown. From a crystal of suitable size we were able to determine the structure of **13**. The ORTEP diagram of **13** is given in Figure 6. It is interesting to find that the I–Co–I angle in **13** is 95.40(8)° and the I–Co–P angles are 91.57(14) and 92.79(14)°. Comparing the corresponding value of 92.70(2)° found in **10** suggests that the triphenylphosphane ligand experiences a smaller repulsive effect compared with the tethered intramolecular coordinated piperidine group. Triphenylphosphane is known as a ligand with a large stereochemical effect and has a cone angle of 143°.[33] However, as a strong σ donor ligand, triphenylphosphane still shows a larger *trans* effect than piperidine. The Co–C(5) bond *trans* to Co–P of 2.141(16) Å is 0.085 Å longer than the *cis* Co–C(3) bond which is 2.056(16) Å. For comparison, the Co–C(2) bond in **10** *trans* to Co–N is 2.086(4) Å, i.e. only 0.053 Å longer than the *cis* Co–C(5) bond which is 2.033(4) Å. There is one iodide counterion hydrogen bonded to the cation through N–H···I interactions with an N···I distance of 3.414(14) Å (Figure 7). This is an almost linear hydrogen bond with d(D–H) = 0.91 Å, d(H···A) = 2.53 Å and <D–H···A = 164.1°. A short contact between the iodide counterions and the hydrogen atom at C(12) adjacent to the nitrogen atom also exists and this should help the molecules pack in the crystal. To the best of our knowledge, this is one of the

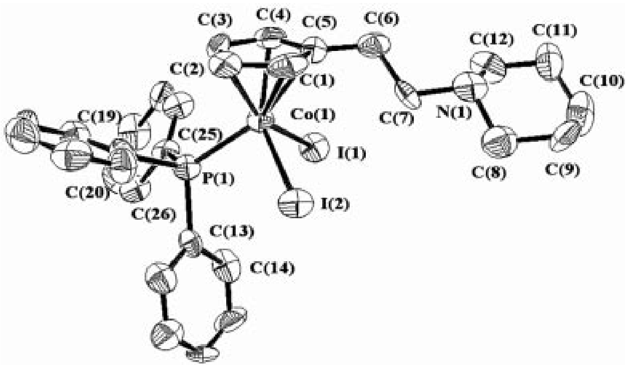


Figure 6. ORTEP diagram of **13** with the probability ellipsoids drawn at the 50% level. Hydrogen atoms, dichloromethane solvate molecule and iodide anion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Average Co–C(ring) 2.094(11), Co(1)–P(1) 2.239(5), Co(1)–I(1) 2.592(3), Co(1)–I(2) 2.568(2), average C–C(ring) 1.40(2), N(1)–C(7) 1.488(19), N(1)–C(12) 1.46(2), I(1)–Co(1)–I(2) 95.40(8), I(1)–Co(1)–P(1) 92.79(14), I(2)–Co(1)–P(1) 91.57(14), Co(1)–P(1)–C(13) 118.0(5), Co(1)–P(1)–C(19) 112.7(7), Co(1)–P(1)–C(25) 115.2(5).

strongest N–H···I hydrogen bonds found in the literature. A similar N–H···I hydrogen bond was found in crystals of $Me_3N·HI$ and it was probably found to be linear with an N···I distance of 3.46(4) Å.[34] A further example can be seen in the crystal structure of the hexakis(*S*,*S*-diphenylsulfimide)cobalt(II) diiodide *S*,*S*-diphenylsulfimide acetonitrile solvate, $[Co(C_{12}H_{11}NS)_6]I_2·C_{12}H_{11}NS·2C_2H_3N$, in which two iodide counterions are hydrogen-bonded to the cation through N–H···I interactions, with N···I distances in the range of 3.7302(19)–3.8461(19) Å and D–H···A angles in the range of 156–172°.[35]

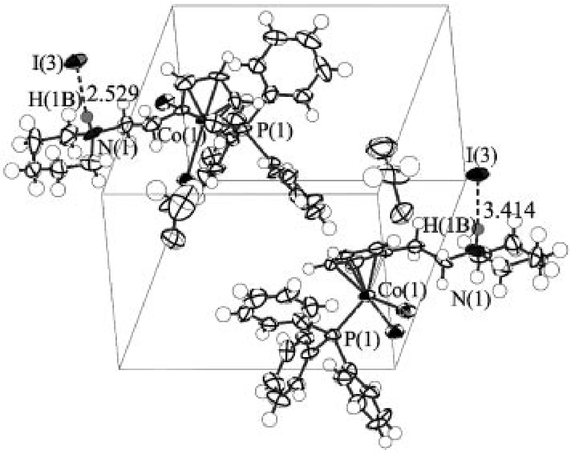


Figure 7. N–H···I hydrogen bonding in the unit cell of complex **13**.

Conclusions

This paper reports the synthesis and reactivity of several cyclopentadienylcobalt complexes having a pendant amino-functionalised side chain. Intramolecular coordination by the pendant amino-functionalised side chain occurs when the oxidation state of the cobalt changes from +I to +III via a diiodocarbonyl intermediate. The stabilities of the intermediates differ greatly due to the different amino functions in the pendant side chains. Structural studies of chelates **9**, **10** and **12** have been carried out and these show that the Co–N bond length does not correlate with the stability of the diiodocarbonyl intermediate precursors but that there exists a correlation between the I–Co–I angles with the repulsive force from the methyl or methylene groups adjacent to the nitrogen atom. The intermediate diiodocarbonyl-η^5-(2-piperidinylethyl)cyclopentadienylcobalt(III) **6′** can be reduced to dicarbonylcyclopentadienylcobalt(I) **6** by the CO released due chelation of the former at a CO concentration of about 0.088 mol L^{-1}. The chelated piperidinyl group in **10** can easily be replaced by triphenylphosphane to form the diiodotriphenylphosphanyl-η^5-(2-piperidinioethyl)cyclopentadienylcobalt(III) iodide dichloromethane solvate **13** in the presence of hydrogen iodide. A strong N–H···I hydrogen bond with a N···I distance of 3.414(14) Å and a D–H···A angle of 164.1° was observed in **13**. It is one of the strongest N–H···I hydrogen bonds reported up to now.

Experimental Section

General: All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques except where mentioned. All reagents were purchased from commercial sources (Acros Organics or Lancaster Synthesis Ltd) in the highest available purity and used as received. Solvents were purified by standard methods and distilled under nitrogen before use. Glassware was heated under vacuum and then flushed with N_2 prior to use. Alumina was heated at 300 °C under vacuum and then deactivated by addition of about 6 wt.-% of deoxygenated water before use.

Elemental analyses were performed on a Vario EL III Elemental Analyaer (Analysensysteme GmbH, Germany). IR spectra were recorded on a Nicolet Avatar-360 FTIR spectrometer in KBr pellets. A 0.2 mm NaCl IR cell was used to record the spectrum of solution samples. ^1H NMR spectra were recorded on a Bruker Avance-DMX 500 NMR spectrometer or a JEOL ECA400 NMR spectrometer. The chemical shifts are reported in ppm relative to tetramethylsilane. Mass spectra were recorded on a Hewlett–Packard (USA) 6890/5073 gas chromatography–mass spectrometer. High resolution matrix assisted laser desorption ionisation mass spectra were recorded on an IonSpec 4.7 Tesla FTMS spectrometer at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, with 2,5-dihydroxybenzoic acid (DHB) serving as the absorbing matrix.

The crystal data were determined on a Bruker Smart-Apex CCD X-ray diffractometer equipped with a graphite monochromator. Data collection was performed with Mo-K_α radiation (λ = 0.71073 Å) using the ω-2θ scan technique to a maximum 2θ value of 26° at room temperature. The intensities were corrected for Lorentz polarisation effects and empirical absorption with the SADABS program.[36] Structures of the crystals were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically with full-matrix least-squares methods. Hydrogen atoms were not included in the refinements. The final agreement factors are described with R_1 and wR_2 values for observed reflections. All calculations were performed on a PC computer using SHELX-97[37] the Bruker Smart program. Crystal data and experimental details for **9**, **10**, **12** and **13** are listed in Table 4 and selected bond lengths and angles are listed under the respective ORTEP diagrams.

Synthesis of Compounds and Complexes

2-Aminoethylcyclopentadiene (1): Freshly distilled THF (50 mL) was added to a 250 mL Schlenk tube containing sodium sand (1.7835 g, 77.58 mmol) and the mixture was cooled in an ice-water bath. Freshly distilled cyclopentadiene (9 mL) was added dropwise and H_2 gas started to bubble out. After 30 min the bubbling stopped and the sodium sand had disappeared. The resultant pink solution was added by cannula to another 150 mL of Schlenk tube containing $BrCH_2CH_2NH_2·HBr$ (4.1 g, 20.21 mmol) in THF (50 mL) which had already been cooled in an ice-water bath. The reaction mixture was then stirred at room temperature for 48 h during which time a white solid precipitated out from the solution. Water (50 mL) was added by cannula to the reaction mixture to dissolve the white precipitate. The organic layer was then separated. The aqueous phase was extracted with hexane (3 × 20 mL). The extract and the organic phase were combined and the volume was reduced to about 15 mL, cooled in an ice-water bath and acidified with aqueous HCl (concentrated HCl/water, 1:4). The separated aqueous phase was added directly to an ice-cold solution made from hexane (20 mL) and aqueous NaOH solution. The basic

Table 4. Crystal data and structure refinement details for **9**, **10**, **12** and **13**.

	9	**10**
Empirical formula	$C_7H_{10}CoI_2N$	$C_{12}H_{18}CoI_2N$
Fw	420.82	489.00
T [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$Pnma$	$P2_1/c$
Unit cell dimensions		
a [Å]	7.393(2)	14.934(4)
b [Å]	11.708(3)	11.805(3)
c [Å]	11.822(3)	16.153(4)
α [°]	90	90
β [°]	90	91.384(4)
γ [°]	90	90
V [Å^3]	1023.2(5)	2846.9(12)
Z	4	8
$\rho_{calcd.}$ [mg m^{-3}]	2.732	2.282
Limiting indices	$-9 \le h \le 8$	$-18 \le h \le 14$
	$-13 \le k \le 14$	$-12 \le k \le 14$
	$-14 \le l \le 12$	$-16 \le l \le 19$
Reflections coll./unique	4402/1062	12945/5599
R_{int}	0.0260	0.0292
Goodness-of-fit on F^2	1.159	0.791
Abs. coeff. [mm^{-1}]	7.653	5.519
Crystal size [mm]	$0.15 \times 0.10 \times 0.10$	$0.15 \times 0.10 \times 0.08$
θ range for data collection [°]	2.45 to 26.00	1.36 to 26.01
R indices	$R_1 = 0.0365$	$R_1 = 0.0275$
$I > 2\sigma(I)$	$wR_2 = 0.0927$	$wR_2 = 0.0427$
R indices	$R_1 = 0.0402$	$R_1 = 0.0453$
for all data[a]	$wR_2 = 0.0949$	$wR_2 = 0.0452$
Largest diff. peak/hole [e A^{-3}]	1.101/–1.208	0.829/–0.738

	12	**13**
Empirical formula	$C_{11}H_{10}CoI_2N$	$C_{31}H_{36}Cl_2CoI_3NP$
Fw	468.93	964.11
T [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)$
Unit cell dimensions		
a [Å]	7.188(3)	11.674(4)
b [Å]	8.157(4)	7.993(3)
c [Å]	11.798(5)	18.581(7)
α [°]	92.976(6)	90
β [°]	91.282(6)	92.043(6)
γ [°]	115.947(4)	90
V [Å^3]	620.4(5)	1732.7(11)
Z	2	2
$\rho_{calcd.}$ [mg m^{-3}]	2.510	1.848
Limiting indices	$-8 \le h \le 8$	$-13 \le h \le 13$
	$-8 \le k \le 9$	$-9 \le k \le 9$
	$-13 \le l \le 14$	$-19 \le l \le 22$
Reflections coll./unique	2615/2164	7306/5608
R_{int}	0.0252	0.0482
Goodness-of-fit on F^2	0.991	0.927
Abs. coeff. [mm^{-1}]	6.326	3.389
Crystal size [mm]	$0.15 \times 0.08 \times 0.05$	$0.15 \times 0.10 \times 0.08$
θ range for data collection [°]	1.73 to 25.01	1.10 to 25.01
R indices	$R_1 = 0.0456$	$R_1 = 0.0641$
$I > 2\sigma(I)$	$wR_2 = 0.1126$	$wR_2 = 0.1493$
R indices	$R_1 = 0.0570$	$R_1 = 0.0974$
for all data[a]	$wR_2 = 0.1182$	$wR_2 = 0.1719$
Largest diff. peak/hole [e A^{-3}]	1.735/–1.392	2.055/–1.536

aqueous phase (pH > 14) was extracted with hexane (3×20 mL). The organic phase and extract were combined, dried with anhydrous $MgSO_4$ and the solvents evaporated to give the product as an oily liquid (0.487 g, 4.46 mmol). Yield: 22.1 %. The resultant oily product was identified as a 1:1 mixture of isomers. ^{1}H NMR ($CDCl_3$): δ = 6.44 (d, J = 1.17 Hz, 1.5 H, =CH), 6.29 (d, J = 4.25 Hz, 0.5 H, =CH), 6.23 (s, 0.5 H, =CH), 6.09 (s, 0.5 H, =CH), 2.98 (s, 1 H, =CHCH−), 2.87–2.91 (m, 3 H, −CH), 2.56 (t, J = 6.7 Hz, 1 H, −CH_2), 2.51 (t, J = 6.7 Hz, 1 H, −CH_2) ppm. GCMS: m/z (%) = 109 (45) [M]$^+$, 80 (100) MH – $CH_2NH_2]^+$; retention times: 8.247, 8.327 min.

(2-Piperidinoethyl)cyclopentadiene (2): The compound was synthesised according to the reported procedure with little modification.[14] The product was purified on an alumina column. The resultant oily product was identified as a 1:1 mixture of isomers and a yield of 40 % was redorded. ^{1}H NMR ($CDCl_3$): δ = 6.45 (s, =CH), 6.42 (s, =CH), 6.27 (s, =CH), 6.19 (s, =CH), 6.05 (s, =CH), 3.59 (t, J = 7.34 Hz, 2 H, −CH_2−), 2.93 (d, J = 16.03 Hz, 1 H, −CH−), 2.69 (t, J = 7.35 Hz, 2 H, −CH_2N), 2.45 (m, 4 H, −NCH_2−), 1.60 (m, 4 H, −CH_2−), 1.46 (m, 2 H, −CH_2−) ppm. ^{1}H NMR ([D$_6$]acetone): δ = 6.42 (s, =CH), 6.21 (s, =CH), 6.03 (s, =CH), 5.94 (s, =CH), 5.47 (s, =CH), 5.11 (d, J = 14.41 Hz, 2 H, −CH_2−), 2.91 (d, J = 7.10 Hz, 1 H, −CH−), 2.50 (m, 2 H, −CH_2N), 2.42 (m, 4 H, −CH_2N), 2.12 (m, 2 H, −NCH_2−), 1.44 (m, 4 H, −CH_2−), 1.24 (m, 2 H, −CH_2−) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 146.58, 144.12, 133.74, 132.59, 131.37, 129.65, 125.82, 125.43, 123.92 (=CH), 58.52, 57.85, 56.79 (CpCH$_2$CH$_2$N−), 53.63 (α-NCH$_2$−), 42.48, 40.25, 33.29 (−CH$_2$−), 27.32, 26.79, 26.57 (CpCH$_2$CH$_2$N−), 25.02, 23.46 (−CH$_2$−) ppm. GCMS: m/z (%) = 177 (25) [M]$^+$, 98 (100) [M – $C_5H_5CH_2]^+$, 80 (10) [MH – $CH_2NC_5H_{10}]^+$; retention times: 10.03, 10.15 min.

1-(2-Piperidinoethyl)-2,3,4,5-tetraisopropylcyclopentadiene (3): $C_5H_{10}NC_2H_4Cl{\cdot}HCl$ (5.174 g, 28.26 mmol) was added to an ice-cold mixture of hexane (30 mL) and aqueous KOH solution. The organic layer containing free $C_5H_{10}NC_2H_4Cl$ was separated and dried with $MgSO_4$. The volume was reduced to about 10 mL and THF (15 mL) was then added. The mixed solution was added by cannula to another 150 mL capacity Schlenk tube containing potassium tetraisopropylcyclopentadienide[19] (7.07 g, 25.8 mmol) and THF (60 mL). The resultant reaction mixture was heated to reflux for 24 h. The reaction was then quenched with water, extracted with hexane and eluted on an alumina column. A yellowish oil was obtained (3.5 g, 10.1 mmol) in a yield of 35.9 %. ^{1}H NMR ($CDCl_3$): δ = 3.16 (m, −CHC−), 2.74 (m, −CHC−), 2.46 (b, −CH_2N), 2.29 (b, −NCH_2), 1.87 (m, −CHMe$_2$), 1.62 (b, −CH_2−), 1.54 (b, −CH_2−), 1.39 (m, −CHMe_2), 1.19 (m, −CHMe_2), 1.12 (m, −CHMe_2), 1.01 (m, −CHMe_2) ppm. GCMS: m/z (%) = 345 (15) [M]$^+$.

2-Picolylcyclopentadiene (4): This compound was synthesised according to the reported procedure.[22] The product was separated on an alumina column. The resultant oily product was identified as 1:1 mixture of isomers. ^{1}H NMR ($CDCl_3$): δ = 8.54 (t, J = 4.80 Hz, 1 H, =CH), 7.59 (m, 1 H, =CH), 7.17 (t, J = 6.88 Hz, 1 H, =CH), 7.11 (t, J = 4.60 Hz, 1 H, =CH), 6.44 (m, =CH), 6.29 (m, =CH), 6.23 (m, =CH), 6.10 (m, =CH), 3.94 (s, −CH_2−), 3.91 (s, −CH_2−), 3.00 (s, −CH−), 2.92 (t, −CH_2−) ppm.

Dicarbonyl-η^5-(2-aminoethyl)cyclopentadienylcobalt(I) (5): **1** (0.612 g, 5.61 mmol) was dissolved in CH_2Cl_2 (20 mL) containing 3,3-dimethyl-l-butene (5 mL) and the solution added by cannula to a CH_2Cl_2 solution (30 mL) containing $Co_2(CO)_8$ (0.6259 g, 1.83 mmol) at 0 °C. The deep red reaction mixture was stirred at ambient temperature and was inspected by observing the two characteristic ν_{CO} bands (2017, 1951 cm^{-1}) in the IR spectrum until their intensities became constant. This took about 24 h. The volume of the reaction mixture was reduced to about 2 mL under vacuum and the resultant solution was loaded on an alumina column and rinsed with 1:1 solvent mixture of THF and hexane. A deep red band was collected and the solvent was evaporated in vacuo. A deep red oily product was obtained (0.34 g). Yield 42.0%. ^{1}H NMR (CDCl$_3$): δ = 5.02 (s, 2 H, =C*H*), 4.92 (s, 2 H, =C*H*), 3.48 (m, 4 H, $-CH_2CH_2-$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3365, 2960, 2016 (C=O), 1951 (C=O), 1598, 1439, 1366, 1261, 1090, 1023, 898, 802 cm^{-1}.

Dicarbonyl-η^5-(2-Piperidinoethyl)cyclopentadienylcobalt(I) (6): A similar synthetic procedure was used as described for complex **5**. Thus Co$_2$(CO)$_8$ (0.976 g, 2.84 mmol) and **2** (1.43 g, 8.07 mmol) were stirred together for 20 h and the resultant mixture passed down an alumina column to produce a deep red oily product (0.226 g). Yield 13.7%. ^{1}H NMR (CDCl$_3$): δ = 5.04 (s, 2 H, =C*H*), 4.90 (s, 2 H, =C*H*), 2.49 (2 H, $-CH_2N-$), 2.43 (4 H, $-NCH_2-$), 2.18 (2 H, $-CH_2-$), 1.60 (4 H, $-CH_2-$), 1.45 (2 H, $-CH_2-$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3401, 2935, 2854, 2800, 2766, 2019 (C=O), 1954 (C=O), 1603, 1445, 1373, 1352, 1262, 1155, 1114, 1039, 862, 802 cm^{-1}.

Dicarbonyl-η^5-1-(2-piperidinoethyl)-2,3,4,5-tetraisopropylcyclopentadienylcobalt(I) (7): A similar synthetic procedure was used as described for complex **5**. Thus Co$_2$(CO)$_8$ (0.4944 g, 1.45 mmol) and **3** (1.00 g, 2.90 mmol) were stirred under reflux for 24 h and the resultant mixture passed down an alumina column to produce a deep red oily product (0.785 g). Yield 59.0%. ^{1}H NMR (CDCl$_3$): δ = 2.44 (s, 2 H, $-CH_2N$), 2.29 (b, 4 H, $-NCH_2$), 1.91 (m, 4 H, $-CHMe_2$), 1.87 (s, 2 H, $-CH_2-$), 1.54 (b, 6 H, $-CH_2-$), 1.26 (m, 6 H, $-CHMe_2$), 1.16 (m, 12 H, $-CHMe_2$), 1.11 (m, 6 H, $-CHMe_2$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3389, 2960, 2932, 2871, 2003 (C=O), 1942 (C=O), 1466, 1381, 1367, 1261, 1155, 1108, 1041, 861, 806 cm^{-1}.

Dicarbonyl-η^5-2-picolylcyclopentadienylcobalt(I) (8): A similar synthetic procedure was used as described for complex **5**. Thus Co$_2$(CO)$_8$ (0.1755 g, 0.513 mmol) and **4** (0.1585 g, 1.01 mmol) were stirred together for 13 h and the resultant mixture passed down an alumina column to produce a deep red oily product (0.098 g). Yield 35.6%. ^{1}H NMR (CDCl$_3$): δ = 8.55 (s, 1 H, =C*H*−N), 7.64 (t, 1 H, =C*H*), 7.26 (t, 1 H, =C*H*), 7.14 (t, 1 H, =C*H*), 5.09 (s, 2 H, Cp), 4.93 (s, 2 H, Cp), 3.75 (s, 2 H, $-CH_2-$) ppm. IR (neat): $\tilde{\nu}_{max}$ = 3400, 3083, 3011, 2956, 2927, 2854, 2016 (C=O), 1948 (C=O), 1591 (C=N), 1570 (C=N), 1475, 1435, 1365, 1309, 1221, 1149, 1092, 1049, 995, 920, 820, 785, 749, 616 cm^{-1}.

Diiodo-η^5:η^1-(2-aminoethyl)cyclopentadienylcobalt(III) (9): To a solution of **5** (0.087 g, 0.39 mmol) in ether (15 mL) was slowly added a solution of iodine (1.00 g, 0.394 mmol) in ether with vigorous stirring. A black-purple precipitate immediately appeared. The reaction mixture was stirred for a further 1 h. The precipitate was filtered and washed with hexane (2× 10 mL) and dried in vacuo. A red-purple solid was obtained (0.171 g). Yield: 97.7%. The solid showed a strong ν_{CO} band at 2068 cm^{-1} which disappeared after about one week. The solid was dissolved in dichloromethane and layered with hexane and a crystalline product was obtained (0.148 g). Yield 90.2%. Crystals suitable for X-ray crystallographic analysis were obtained from that crop. C$_7$H$_{10}$CoI$_2$N (420.823): calcd. H 2.39, C 19.96, N 3.33; found H 2.44, C 19.86, N 3.41. ^{1}H NMR (CDCl$_3$): δ = 5.51 (t, 2 H, =C*H*), 5.27 (t, 2 H, =C*H*), 4.22 (t, J = 5.48 Hz, 2 H, $-CH_2N-$),2.42 (t, J = 6.42 Hz, 2 H, $-CH_2N-$) ppm. MS (HiRMALDI): *m/z* (%): 573.2 (3.0) [M + DHB – H]$^+$, 545.2 (32) [M + DHB – CH$_2$NH$_2$]$^+$, 438.2 (8.0) [M + H$_2$O – H]$^+$, 293.1 (26.0) [M – I – H]$^+$. IR (KBr pellet): $\tilde{\nu}_{max}$ = 3192, 2961, 1571, 1459, 1310, 1263, 1120, 1035, 1013, 840, 734, 700.2 cm^{-1}. UV/Vis (CH$_3$CN): λ_{max} (ε) = 247 (7.61 × 10^3), 290 (1.04 × 10^4), 360 (4.03 × 10^3), 585 (4.53 × 10^2) nm.

Diiodo-η^5:η^1-(2-piperidinoethyl)cyclopentadienylcobalt(III) (10): A similar synthetic procedure was used as described for complex **9**. Thus **6** (0.226 g, 0.776 mmol) in ether (15 mL) was added to iodine (0.1985 g, 0.782 mmol) in ether (15 mL) and the solution stirred overnight. The resultant green-black precipitate was washed with hexane until the washings became colourless. The solid showed a medium strong ν_{CO} band at 2059 cm^{-1} which disappeared after about 12 h. The solid was dissolved in dichloromethane and filtered through a pad of celite and the solvent was then evaporated. A green-black solid was obtained (0.204 g). Yield 53.8%. Crystals suitable for X-ray crystallographic analysis were obtained from a sample dissolved in dichloromethane and layered with hexane. C$_{12}$H$_{18}$CoI$_2$N (489.02): calcd. H 3.71, C 29.47, N 2.86; found H 3.61, C 29.58, N 2.71. ^{1}H NMR (CDCl$_3$): δ = 5.46 (s, 2 H, =C*H*), 5.19 (s, 2 H, =C*H*), 4.41 (t, J = 6.40 Hz, 2 H, $-CH_2N-$), 3.52 (d, J = 13.7 Hz, 2 H, $-NCH_eH_a-$), 2.93 (t, J = 13.7 Hz, 2 H, $-NCH_eH_a-$), 2.51 (t, J = 6.40 Hz, 2 H, $-CH_2-$), 1.72 (m, 4 H, $-CH_2-$), 1.22 (m, 2 H, $-CH_2-$) ppm. ^{1}H NMR ([D$_6$]acetone): δ = 5.69 (s, 2 H, =C*H*), 5.11 (s, 2 H, =C*H*), 4.49 (t, J = 6.40 Hz, 2 H, $-CH_2N-$), 3.61 (d, J = 13.3 Hz, 2 H, $-NCH_eH_a-$), 2.81 (t, J = 13.3 Hz, 2 H, $-NCH_eH_a-$), 2.68 (t, J = 6.40 Hz, 2 H, $-CH_2-$), 1.90 (m, 4 H, $-CH_2-$), 1.13 (m, 2 H, $-CH_2-$) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 112.93 (CpCH$_2-$), 83.49 (Cp), 81.38 (Cp), 65.50 ($-CH_2CH_2N-$), 61.10 (*ortho*-NCH$_2-$), 25.39 (CpCH$_2$CH$_2$N−), 24.32, 22.30 ($-CH_2-$) ppm. MS (HiRMALDI): *m/z* (%): 514.9 (12.5) [M + DHB – I – H]$^+$, 422.9 (4.0) [M + H$_2$O – NC$_5$H$_{10}$]$^+$, 379.1 (23) [M + H$_2$O – I – H]$^+$, 362.0 (10) [M – I]$^+$. IR (KBr pellet): $\tilde{\nu}_{max}$ = 3076, 2932, 2856, 2801, 1726, 1603, 1468, 1443, 1393, 1353, 1309, 1261, 1101, 1025, 802 cm^{-1}. UV/Vis (CH$_3$CN): λ_{max} (ε) = 248 (1.01 × 10^4), 286 (7.06 × 10^3), 587 (5.79 × 10^2) nm.

Diiodo-η^5:η^1-1-(2-piperidinoethyl)-2,3,4,5-tetraisopropylcyclopentadienylcobalt(III) (11): A similar synthetic procedure was used as described for complex **9**. Thus **7** (0.786 g, 1.71 mmol) in ether (35 mL) was added to iodine (0.4456 g, 1.76 mmol) in ether (10 mL) and the resultant mixture stirred overnight. A red-purple solid precipitated which showed a medium-strong ν_{CO} band at 2046 cm^{-1}. The solid was dissolved in dichloromethane and filtered through a pad of celite and the solvent subsequently removed in vacuo. A solid was obtained (0.165 g). Yield 15%. C$_{24}$H$_{42}$CoI$_2$N (657.35): calcd. H 6.44, C 43.85, N 2.13; found H 6.96, C 44.70, N 1.91. ^{1}H NMR (CDCl$_3$): δ = 1.72 (d, 6 H, $-CH_3$), 1.70 (d, 6 H, $-CH_3$), 1.53 (d, $-CH_3$), 1.50 (d, 6 H, $-CH_3$), 2.05 (m, 4 H, Me$_2$C*H*), 3.83 (s, 2 H, $-CH_2N-$), 3.65 (s, 4 H, $-NCH_eH_a-$), 3.32 (s, 2 H, $-NCH_eH_a-$), 3.18 (s, 4 H, $-CH_2-$), 2.37 (m, 4 H, $-CH_2-$) ppm.

Diiodo-η^5:η^1-2-picolylcyclopentadienylcobalt(III) (12): A similar synthetic procedure was used as described for complex **9**. Thus complex **8** (0.098 g, 0.359 mmol) in hexane (10 mL) was added to iodine (0.097 g, 0.382 mmol) in hexane (10 mL) and the mixture stirred for 24 h. The resultant dark green precipitate was separated and washed twice with hexane and dissolved in dichloromethane. The solution was filtered and the solvent removed in vacuo. A dark green solid was obtained (0.1615 g). Yield 96.0%. Crystals suitable for X-ray crystallographic analysis were obtained from a sample dissolved in dichloromethane and crystallised by layering with hexane. C$_{11}$H$_{10}$CoI$_2$N (468.831): calcd. H 2.15, C 28.16, N 2.99; found H 2.168, C 28.29, N 2.886. ^{1}H NMR (CDCl$_3$): δ = 7.97 (s, 1 H, =C*H*−N), 7.70 (t, 1 H, =C*H*), 7.16 (d, 1 H, =C*H*), 7.00 (t, 1 H, =C*H*), 5.73 (s, 2 H, Cp), 5.38 (s, 2 H, Cp), 4.09 (s, 2 H, $-CH_2-$) ppm. MS (HiRMALDI): *m/z* (%): 341.9 (10.0) [M – I]$^+$. IR (KBr pellet): $\tilde{\nu}_{max}$ = 3090, 2960, 2924, 2858, 1605 (C=N), 1470, 1439, 1417, 1391, 1262, 1151, 1102, 1048, 1021, 846, 764 cm^{-1}. UV/

Vis (CH_3CN): λ_{max} (ε) = 246 (7.51×10^3), 286 (5.28×10^3), 405 (6.32×10^2), 593 (5.63×10^2) nm.

Diiodotriphenylphosphanyl-η^5-(2-piperidinioethyl)cyclopentadienylcobalt(III) Iodide ($C_5H_4C_2H_4NHC_5H_{10}CoI_2PPh_3$)$^+$ I$^-$·CH_2Cl_2 (13): To a stirred solution of **6** (0.120 g, 0.412 mmol) in dichloromethane (10 mL) was added iodine (0.220 g, 0.887 mmol) in dichloromethane (10 mL) and the resultant mixture was stirred for 4 h. A solution of triphenylphosphane (0.2326 g, 0.885 mmol) in dichloromethane was then added at room temperature. The reaction mixture was stirred continuously for another 24 h under room temperature. The volume of the solvent was reduced in vacuo and hexane was layered over the remaining dichloromethane solution. Brown-black needle-shaped crystals formed several days later and 0.187 g of crystallised product was separated by filtration. Crystals suitable for X-ray crystallographic analysis were obtained. Structural analysis demonstrates that a solvent molecule of dichloromethane is incorporated in the crystal lattice. The resultant product was thus formulated as ($C_5H_4C_2H_4NHC_5H_{10}CoI_2PPh_3$)$^+$ I$^-$·CH_2Cl_2. Based on this composition, the yield was 47% ^{1}H NMR ($CDCl_3$): δ = 7.23–7.90 (m, 15 H, Ph), 5.45 (s, 2 H, =CH), 5.30 (s, 2 H, CH_2Cl$_2$), 4.08 (m, 2 H, $-CH_2N-$), 3.97 (m, 2 H, $-NCH_2-$), 3.93 (s, 2 H, =CH), 3.82 (m, 2 H, $-NCH_2-$), 3.00 (m, 2 H, $-CH_2-$), 2.63 (s, 1 H, $-NH-$), 2.34 (m, 2 H, $-CH_2-$), 1.97 (m, 4 H, $-CH_2-$) ppm. IR (KBr pellet): $\tilde{\nu}_{max}$ = 3432, 3054, 2960, 2925, 2854, 1605, 1434, 1379, 1264, 1091, 1026, 800, 741, 697 cm^{-1}. UV/Vis (CH_3CN): λ_{max} (ε) = 232 (1.65×10^4), 279 (7.70×10^3), 585 (8.07×10^2) nm.

Reduction with CO: Reaction intermediate **6′** was synthesised in situ. To a solution of **6** (0.157 g, 0.539 mmol) in dichloromethane (0.90 mL) was added iodine (0.141 g, 0.556 mmol) in dichloromethane (0.85 mL) with vigorous stirring for half a minute. The reaction mixture was then transferred to an IR cell which had been flushed with N_2 before use. The chamber of the IR cell was fully filled with the reaction mixture and tightly sealed with a Teflon stopper, no empty space was allowed. The first spectrum was measured 2 min after the iodine was added. The carbonyl absorption bands were monitored and the spectra were recorded. Plots of ln$A$ vs. t for the absorbance of the monocarbonyl intermediate were linear over 2 half-lives [log$A$(2066 cm^{-1}) = –0.0975–$6.394 \times 10^{-4}t$, R_2 = –0.9997] after 882 s. From a another sample of **6** in dichloromethane, the absorbances of the carbonyl were found to be linear in the concentration range from 0.04 to 0.16 M [A(2017 cm^{-1}) = 0.00782 + 5.232(Co^I), R_2 = 0.9999; A(1953 cm^{-1}) = 0.00551 + 4.869(Co^I), R_2 = 0.9999]. The calculations of the concentrations of the diiodomonocarbonyl intermediate **6′** and the formed dicarbonyl product **6** listed in Table 3 are based on these linear relationships.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC-615490 (for **9**), -615491 (for **10**), -615492 (for **12**) and -615489 (for **13**), respectively.

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