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Preparation of cationic cobalt phenoxide and ethoxide complexes and their reversible reaction with carbon dioxide

Stephen J. Archibald,[a] Simon P. Foxon,[b] Jonathan D. Freeman,[b] James E. Hobson,[b] Robin N. Perutz *[b] and Paul H. Walton *[b]

[a] *Department of Chemistry, University of Hull, Cottingham Road, Hull, England HU6 7RX*
[b] *Department of Chemistry, University of York, Heslington, York, England Y010 5DD. E-mail: phw2@york.ac.uk*

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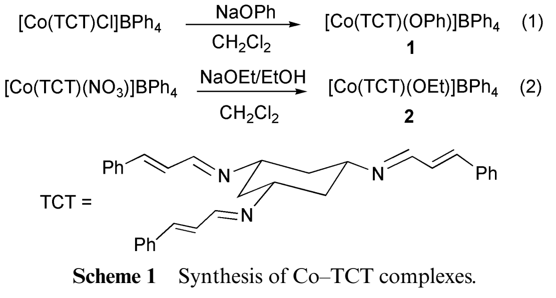
The complexes [Co(TCT)(OR)]BPh$_4$ (R = Et, Ph; TCT = *cis*,*cis*-1,3,5-tris(cinnamylideneamino)cyclohexane) have been prepared and characterised by X-ray diffraction; in coordinating solvents both complexes react reversibly with carbon dioxide to form organocarbonate complexes.

Metal alkoxide complexes find use in a variety of reactions, including ring-opening polymerisation of lactides,[1] transesterification,[2] and copolymerisation of carbon dioxide and epoxides.[3] In addition, recent work on modelling the active site of horse liver alcohol dehydrogenase has involved the synthesis of monomeric zinc alkoxides.[4] Monomeric, cationic metal alkoxide complexes are difficult to isolate due to potential hydride abstraction,[5] formation of bridged alkoxy metal species, and the tendency of other anions to coordinate to the metal ion to give neutral complexes. We have previously reported evidence that the monomeric complex [Co^{II}(TCT)(OEt)]BPh$_4$ catalyses the decomposition of dialkylpyrocarbonates.[6] Here we report the analogous cobalt(II) phenoxide complex, and show that both complexes react reversibly with CO$_2$. We also report the isolation and structure of the cobalt ethoxide — the first structure of a monomeric, cationic cobalt(II) alkoxide.

[Co(TCT)(OPh)]BPh$_4$ (**1**) and [Co(TCT)(OEt)]BPh$_4$ (**2**) were prepared in good yield by stirring a dichloromethane solution of [Co(TCT)Cl]BPh$_4$ with solid NaOPh·3H$_2$O, and [Co(TCT)(NO$_3$)]BPh$_4$ with a solution of NaOEt in ethanol, respectively (eqns. (1) and (2), Scheme 1). The complexes could also be prepared by addition of phenol or ethanol to a solution of [Co(TCT)(OH)]BPh$_4$. Both complexes are stable to air in the solid state.†



Scheme 1 Synthesis of Co–TCT complexes.

The crystal structure of **2** is shown in Fig. 1.‡ In both, the cobalt adopts a C_{3v} coordination geometry, with the three nitrogen atoms of the TCT ligand capping one face of the metal. The fourth coordination site is occupied by the aryloxide/alkoxide group, which is bound *via* the oxygen atom. The C–O vector of the ethoxide group is directed between two of the cinnamyl arms, and "*trans*" to the third. The cinnamyl arms of the TCT ligand create a hydrophobic pocket that encapsulates the aryloxide/alkoxide group. There are no contacts less than 4.4 Å between the aromatic rings of the TCT and phenoxide ligands in **1**, nor are there any contacts less than 4.7 Å between the cations, indicating that there are no π–π interactions.

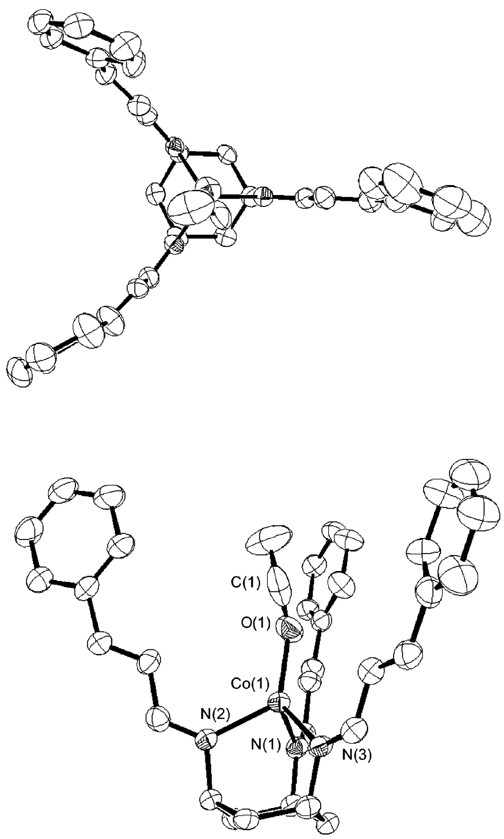


Fig. 1 ORTEP[10] (50% probability ellipsoids) views of **2**. Selected bond lengths/Å: Co–O 1.867(4), Co–N1 2.014(4), Co–N2 2.027(4), Co–N3 2.019(4); Bond angles/°: O–Co–N1 115.1(2), O–Co–N2 125.8(2), O–Co–N3 123.0(2), Co–O–C1 136.8(5). BPh$_4^-$ and H atoms deleted for clarity.

The visible spectrum of **1** in dichloromethane (Fig. 2a) shows absorptions at 507, 523 (sh), 561 and 641 nm. The bands are shifted by less than 1 nm upon changing the solvent to [9CH$_2$Cl$_2$: 1MeOH] v/v or [9CH$_2$Cl$_2$: 1EtOH] v/v. On dissolving **1** in CH$_3$CN, the band previously at λ = 507 nm shifts to λ = 517 nm, but the remaining bands are hardly affected. The insensitivity of the spectrum to solvent, and the absorption coefficients (450–600 dm^3 mol^{-1} cm^{-1}), suggest that the absorptions are predominantly due to d–d transitions.

A dichloromethane solution of **1** showed no colour change or alteration in its visible spectrum after passing a stream of carbon dioxide through it for extended periods. When a stream of carbon dioxide (99.995%) was passed through a solution of **1** dissolved in the mixed solvent [9CH$_2$Cl$_2$: 1MeOH] v/v, an immediate colour change from reddish-purple to orange

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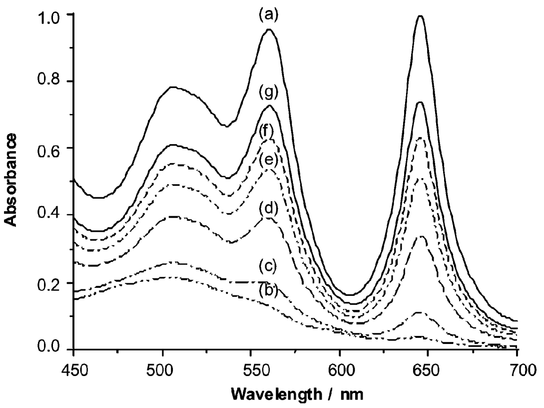


Fig. 2 UV/vis spectra showing (a) **1** under N_2 initially, (b) CO_2 bubbled for 60 s, (c)–(g) N_2 bubbled for 30, 45, 60, 90 and 120 s.

occurred, which could be monitored by visible spectroscopy (Fig. 2). The structure of the visible spectrum changes dramatically, and the intensities of the absorptions decrease substantially after reaction with carbon dioxide (Fig. 2b). The new spectrum exhibits absorptions at 471 nm (sh), 501 nm, 556 nm (sh) and 644 nm. Reaction is still observed on stirring with a partial pressure of only 10 Torr CO_2. Upon passing a stream of inert gas (N_2 or Ar) through the carbonated solution, the colour reverted to reddish-purple, and the original visible spectrum for **1** was obtained (Figs. 2c–g). The carbonated species **3**, when protected from light, does not decolourise in solution over extended periods.

IR spectra show the appearance of bands at 1327 and 1093 cm^{-1} upon reaction with carbon dioxide. Other bands shift slightly (Fig. 3b,d) and a further new band may be present at

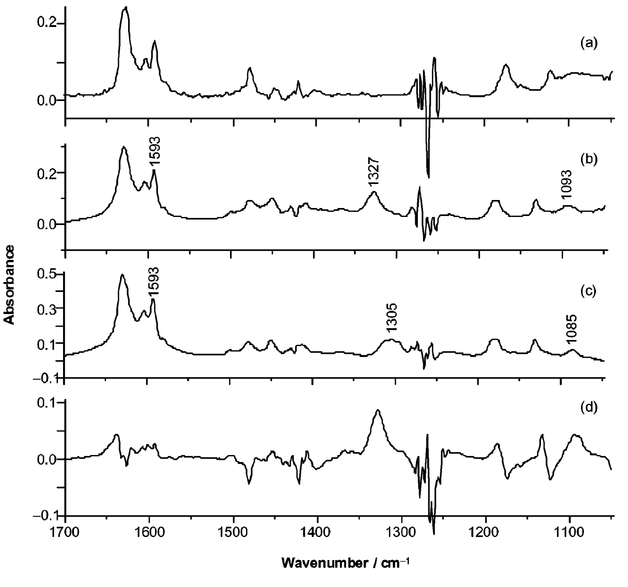


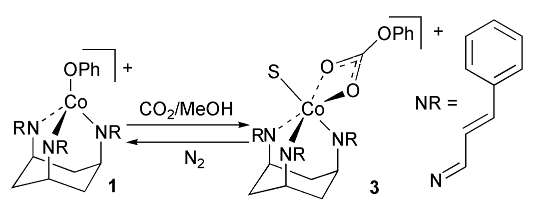
Fig. 3 Solution ([9CH$_2$Cl$_2$: 1MeOH] v/v) FTIR spectra of **1** (a) before CO_2, (b) after $C^{16}O_2$, (c) after $C^{18}O_2$, (d) b − a. The regions 1250–1280 and 1390–1440 cm^{-1} are noisy due to strong solvent absorption.

1593 cm^{-1}, but is masked by a precursor band. The IR spectrum after $C^{18}O_2$ exposure (Fig. 3c) shows that the absorption at 1327 cm^{-1} shifts to 1305 cm^{-1}, and the absorption at 1093 cm^{-1} shifts to 1085 cm^{-1}.

The IR spectrum of **3** correlates very well with three of the four bands characteristic of bidentate organocarbonate complexes (≈1560 cm^{-1}, ≈1460 cm^{-1}, ≈1360 cm^{-1} and ≈1085 cm^{-1}).[7] The solvent "cut-off" region observed between 1440–1390 cm^{-1} could have obscured a fourth band. An analogous experiment in CD_3CN instead of CH_2Cl_2–MeOH gave bands at 1503, 1363 and 1224 cm^{-1}, and a possible band at 1472 cm^{-1}. (Solvent cut-off is < 1110 cm^{-1}.) For both solvents the IR data are consistent with a bidentate organocarbonate complex, but a monodentate complex cannot be excluded. There is already extensive documentation for the conversion of alkyl/aryloxides and their precursors to alkyl/arylcarbonate complexes, but the facile reversible reaction with CO_2 at room temperature is remarkable.[7,8] A very recent paper describes the reaction of CO_2 and cobalt(II) perchlorate with a dinucleating ligand in MeOH–CH_3CN to form a dicobalt methylcarbonato complex. A methoxide complex is a presumed intermediate.[9]

Evidence which shows that CO_2 inserts reversibly into the Co–O bond of complex **2** as well as **1** is provided by visible spectroscopy.§ A solution of **2** in the mixed solvent [9CH$_2$Cl$_2$: 1EtOH] v/v shows a change in the visible spectrum after a stream of carbon dioxide is passed through it for 60 s. The solution progressively regains its original spectrum as a stream of Ar is passed through it.

The requirement for a coordinating solvent (S = MeOH/EtOH/CH_3CN) and the change in the IR spectrum from CH_2Cl_2–MeOH to CD_3CN indicate that solvent is coordinated in the product. A coordinating solvent may facilitate the bidentate coordination of phenylcarbonate to form a six-coordinate cobalt(II) complex from a pseudo-tetrahedral one. The reduced absorption coefficient of **3** compared to **1** is consistent with an octahedral geometry for **3**. We therefore assign the orange carbonated product **3** as [Co(TCT)(S)(η^2-O$_2$COPh)]BPh$_4$ (Scheme 2). Attempts to isolate **3** were unsuccessful. All attempts at crystallization yielded **1**. Evaporating the solvent with a stream of carbon dioxide also led to formation of **1**.



Scheme 2 Reversible reaction of **1** with CO_2.

These studies demonstrate that monomeric cationic alkoxides and aryloxides of cobalt(II) may be isolated with the aid of suitable co-ligands that offer steric protection and a hydrophobic environment. The reversibility of the reaction with CO_2 offers potential for the development of a carbon dioxide sequestration catalyst. Studies by others of metal alkoxide complexes reacting with carbon dioxide show similarities to the work described here. The importance of an auxiliary ligand for coordination sphere expansion has been demonstrated by Saegusa's work on copper complexes.[8a] Furthermore complexes **1** and **3** resemble Vahrenkamp's Zn(Tp) complexes most closely in structure although the two systems differ in their activity towards carbon dioxide.[8e]

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Notes and references

† Complex **1** — [Co(TCT)Cl]BPh$_4$ (0.100 g, 0.11 mmol) was dissolved in CH_2Cl_2 (20 mL). NaOPh (0.050 g, 0.43 mmol) was added, and the mixture was stirred. Within 10 minutes the solution had turned purple. The mixture was left stirring overnight to ensure complete reaction. The solids were filtered off, the solution volume reduced to ≈10 mL, and cyclohexane (20 mL) added to give a reddish-purple precipitate. The liquid was filtered off, and the solid dried *in vacuo*. Yield: 74 mg (0.078 mmol, 69%). Crystals suitable for X-ray diffraction were formed as cyclohexane diffused into a solution of **1** in CH_2Cl_2. Elemental analysis: C: 79.71; H: 6.49; N: 4.19% (calculated for $C_{63}H_{58}N_3CoOB$: C: 80.24; H: 6.21; N: 4.46%). UV/vis: λ_{max}/nm (CH_2Cl_2) 641 (ε/dm^3 mol^{-1} cm^{-1} 600), 561 (530), 523 (sh), 507 (450). IR/cm^{-1}: [DRIFT] 8200 (br), 6250 (br), 4000 (br), d–d transitions; [FTIR] ν(CN) = 1625; ν(CC, aromatic) = 1602; ν(CC, alkenic) = 1590. Mass spectrum: [ESMS] m/z^+ = 623 (M^+); [HRFABMS] m/z^+ = 623.2345 (calculated for $C_{39}H_{38}N_3CoO$: 623.2347, difference = 0.2 mDa).

Complex **2** — [Co(TCT)(NO$_3$)]BPh$_4$ (0.50 g, 0.55 mmol) was dissolved in CH_2Cl_2 (30 mL) in a Schlenk tube under argon. To this was added 3.75 mL of a solution of NaOEt in EtOH (37.5 mg, 0.55 mmol NaOEt); the resulting mixture was shaken for 15 minutes during which time a slight colour change was noted (dark purple to mid-purple). The solution was transferred through a cannula filter to a clean Schlenk tube, and the volatiles removed *in vacuo* to give a purple powder. Yield: 365 mg (0.41 mmol, 74%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a concentrated solution of the complex in CH_2Cl_2/EtOH in a glovebox. UV/vis: λ_{max}/nm ($9CH_2Cl_2$: 1EtOH) 635 (ε/dm^3 mol^{-1} cm^{-1} 239), 554 (362), 486 (291). IR/cm^{-1}: [FTIR] ν(CN) = 1628, ν(CC, aromatic) = 1604, ν(CC, alkenic) = 1593. Mass spectrum: [ESMS] $m/z^+ = 575$ (M^+).

‡ Crystal structure determination of complex $(\mathbf{1})_2(C_6H_{12})_2(CH_2Cl_2)_3$. $C_{141}H_{146}B_2Cl_6Co_2N_6O_2$, M = 2308.2, triclinic, space group $P\bar{1}$, a = 18.31(3), b = 22.022(11), c = 17.219(6) Å, α = 98.97(4), β = 92.61(7), γ = 67.78(5)°, V = 6348 Å^3, T = 150 K, Z = 2, D_c = 1.208 Mg m^{-3}, μ(Mo-Kα) = 0.71069 mm^{-1}, F(000) = 2432, 12510 reflections measured, 11978 unique (R_{int} = 0.10152) which were used in all calculations. $R1$ = 0.0642 on $F > 4\sigma(F)$, $wR2$ = 0.2534 (all data).

Crystal structure determination of complex **2**·0.5(EtOH). $C_{60}H_{61}N_3CoO_{1.5}B$, M = 917.86, triclinic, space group $P\bar{1}$, a = 11.053(2), b = 15.812(3), c = 16.503(3) Å, α = 65.866(12), β = 86.349(14), γ = 72.640(14)°, V = 2506.6(8) Å^3, T = 150(2) K, Z = 2, D_c = 1.216 Mg m^{-3}, μ(Mo-Kα) = 0.387 mm^{-1}, F(000) = 972, 47525 reflections measured, 14596 unique (R_{int} = 0.1698) which were used in all calculations. $R1$ = 0.0901 on $F > 2\sigma(F)$, $wR2$ = 0.2510 on all data. CCDC reference numbers 185609 and 185610. See http://www.rsc.org/suppdata/dt/b2/b204560e/ for crystallographic data in CIF or other electronic format.

§ Reaction of **2** with CO_2: A solution of **2** (10 mg, 11 μmol) in 5 mL of the mixed solvent [$9CH_2Cl_2$: 1 EtOH] v/v was placed in a UV/vis cell under argon, and the visible spectrum recorded. A stream of CO_2 was passed through the solution for 60 s, and the new visible spectrum recorded. Nitrogen was bubbled through the solution and visible spectra were recorded at intervals of 1, 5, 7, 11 and 25 min. Absorption bands of reaction product of **2** with CO_2 λ/nm: 492(sh), 520, 550.

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