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Preliminary communication

SYNTHESIS OF $(CH_3C(CH_2PPh_2)_3)CoL$ COMPLEXES ($L = O_2CO$, S_2CO, O_2SO) THROUGH METAL-ASSISTED CO_2, CS_2, SO_2 OXIDATION. CRYSTAL STRUCTURE OF $(CH_3C(CH_2PPh_2)_3)Co(O_2SO)$

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Summary

The solution obtained by reduction of $[(\text{triphos})Co(\mu\text{-}Cl)_2Co(\text{triphos})]^{2+}$ (triphos $= CH_3C(CH_2PPh_2)_3$) with Na/Hg reacts with CO_2, CS_2 and SO_2 to give (triphos)-$Co(O_2CO)$, (triphos)$Co(S_2CO)$, and (triphos)$Co(O_2SO)$, respectively. The molecular structure of the last has been established by X-ray difraction.

The (triphos)M fragments, where M = Co, Ni, Rh, Pd, Ir, Pt and triphos is the tripod like terdentate ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane, have been found able to activate a large variety of small molecules or stabilize small groups of atoms which cannot exist by themselves [1]. Such ability is mainly due to the particular geometry of the triphos ligand, which, on the one hand bonds the metal only in a facial coordination and on the other hand is unable by itself to saturate the metal centre.

Recently we reported [2] that the reduction of $[(\text{triphos})Co(\mu\text{-}Cl)_2Co(\text{triphos})]^{2+}$ in THF solution with sodium amalgam under nitrogen * generates a deep red-brown solution, **1**, from which addition of n-butanol leads to precipitation of the paramagnetic cobalt(0) dimer $[(\text{triphos})Co\text{-}(\mu\text{-}N_2)Co(\text{triphos})]$ (Scheme 1).

We now report an investigation of the reactions of solution **1** with CO_2, CS_2 and SO_2. The results are summarized in Scheme 2. All the reactions are quite rapid: bubbling of the gas leads immediately either to the precipitation of the derivative (CO_2) or to a sharp colour change (CS_2, SO_2).

Complex **4** was easily identified by elemental analysis and comparison of its IR spectrum and its unit dimensions with those of the known complex (triphos)Co-(S_2CO) [3].

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* When the reaction was performed under argon an analytically ill-defined material was always obtained.

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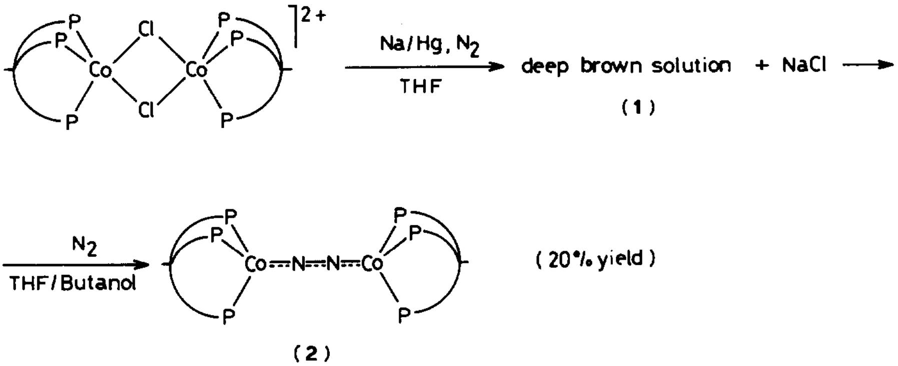
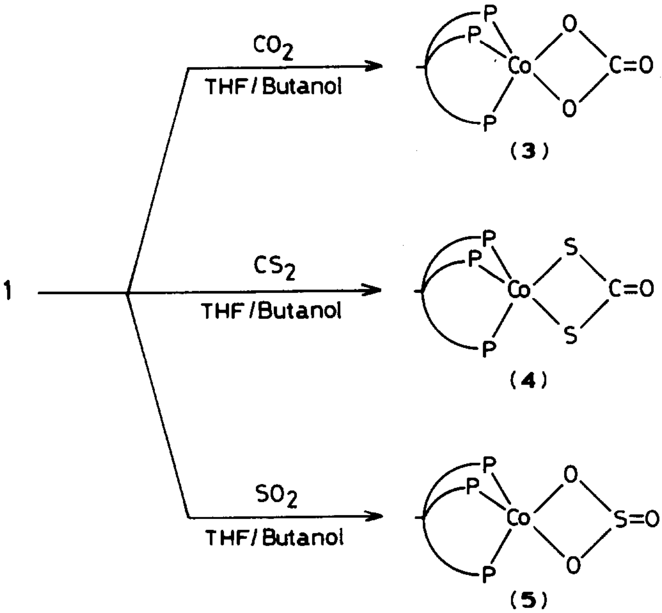


SCHEME 1.



SCHEME 2.

Complexes 3 and 5 were isolated as yellow and brown crystals, respectively, which slowly decompose in air. The solids are paramagnetic with $\mu_{\mathrm{eff}} = 1.94$ and 2.12 BM, respectively, at room temperature, indicative of one unpaired electron on the metal atom. The visible spectra of the two derivatives are quite similar (Fig. 1), and attributable to a low spin cobalt(II) five-coordinate geometry [1,4]. The IR spectrum of 3 shows bands at 1665(vs), 1640(vs), 1205 cm^{-1} which can be attributed to the stretching mode of a bidentate CO_3 group [5].

A complete X-ray crystal structure was carried out on 5. The crystals, which are isomorphous with those other [(triphos)ML] species [3] (L = halogen, BH_4, S_2CO, HCO_2^-, etc.), are orthorhombic, space group $Pn2_1a$, with a 20.503(9), b 17.314(8), c 10.300(5) Å, and $Z = 4$. Data collection was carried out with a Philips PW1100

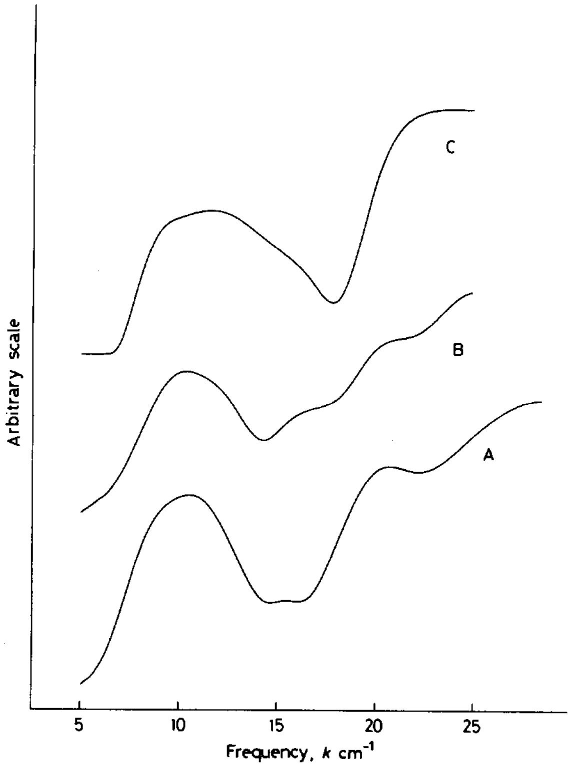


Fig. 1. Solid-state spectra (arbitrary scale) of [(triphos)Co(O_2CCH_3)](BPh_4) [4] (curve A), (triphos)Co(O_2SO) (curve B), (triphos)Co(O_2CO) (curve C).

automatic diffractometer using the ω–2θ scan technique and graphite monochromated Mo-K_α radiation within $2\theta \leq 50°$. Full-matrix least squares refinement converged at R and R_w of 0.069 and 0.065 for the 926 absorption corrected reflections having $I \geq 3\sigma(I)$. The polar axis direction was determined by applying the anomalous dispersion correction [6] *.

The molecular structure consists of monomeric (triphos)Co(O_2SO) units (see Fig. 2). The metal atom is surrounded, in a five coordinated environment, by the three phosphorus atoms of the triphos ligand and two oxygen atoms of the SO_3 group. The coordination can be regarded as a very distorted square pyramid, the distortion from the ideal geometry being indicated by the values of the basal angles, (158.3(9) and 153.5(9)°). The SO_3^{2-} group, acting as bidentate ligand through two oxygen atoms, shows a distorted pyramidal geometry, with a'bite' angle of 90.4(20)°. The average Co–P bond lengths falls in the range of values found for a variety of (triphos)Co five-coordinated complexes [7].

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

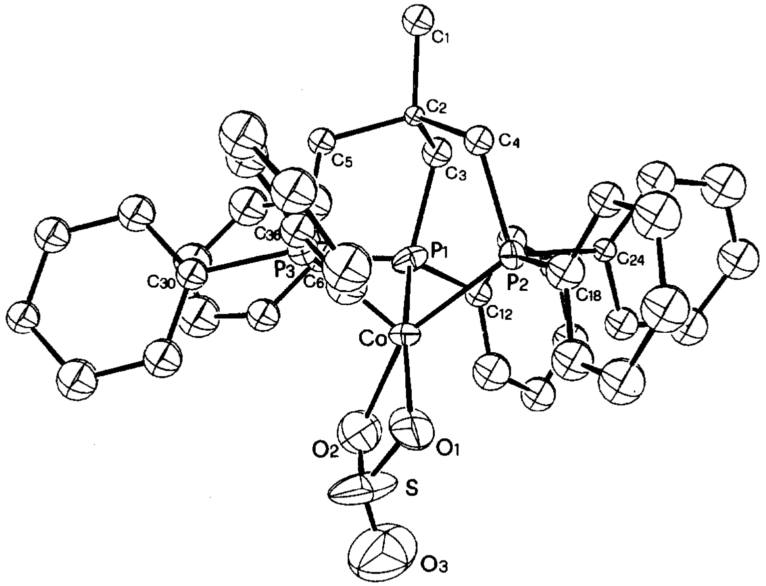

Fig. 2. Perspective view of (triphos)Co(O_2SO). Selected bond distances (Å) and angles (°): Co–P(1) 2.237(9), Co–P(2) 2.236(8), Co–P(3) 2.288(9), Co–O(1) 1.80(4), Co–O(2) 1.91(3), S–O(1) 1.36(3), S–O(2) 1.49(4), S–O(3) 1.13(4); P(1)–Co–O(1) 158.3(9), P(2)–Co–O(2) 153.5(9), O(1)–Co–O(2) 66.1(15), O(1)–S–O(2) 90.4(20), O(1)–S–O(3) 125.9(33), O(2)–S–O(3) 109.5(34).

The synthesis of the complexes **3**, **4**, **5** merits comment. Whereas dismutation processes may be invoked for the formation of CO_3 and SO_3 from CO_2 and SO_2 [8], the oxidation of CS_2 to S_2CO requires an external source of oxygen. On the other hand the three processes appear to be fairly closely analogous.

In order to explore the question, CO_2, CS_2 or SO_2 were bubbled through solutions obtained by dissolving **2** in THF or benzene. Under these conditions reaction was not immediate, and it was only after several hours that, following addition of butanol and evaporation of the solvent under a current of nitrogen, very small amounts of **3**, **4** or **5** derivatives were obtained.

These results strongly suggest that CO_2, CS_2, or SO_2 form the products **3**, **4**, **5** respectively by treatment not with **2** but with another derivative, also present in solution **1**. It is possible that an oxygenated complex is formed by reaction of **2** with traces of molecular oxygen or with adventitious moisture. This possibility is supported by the following findings: (i) **2** is smoothly formed, although only in low yield, by use of Schlenk tube tecniques (Scheme 1); (ii) when the reduction is performed under a stream of nitrogen work-up of the deep red-brown solutions so obtained do not always lead to precipitation of significant amounts of **2**; (iii) these latter solutions always react with CO_2, CS_2, and SO_2 in a similar manner.

The hypothetical oxygenated species * could transfer an oxygen atom to the polar groups CO_2, CS_2, and SO_2 to form the derivatives **3**, **4**, and **5**. It seems very

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* All the attempts to isolate such a species failed. Addition of stoichiometric amounts of oxygen gas or water to the reduced solutions **1**, invariably caused rapid decomposition. Probably extremely high dilution conditions are necessary for generation of such an oxygenated species.

unlikely that there is oxygen transfer to the possible metal complexes (triphos)Co(CO_2), (triphos)Co(CS_2) and (triphos)Co(SO_2) because: (i) it is normally difficult to obtain CO_2-metal complexes; (ii) we have never observed the formation of the known (triphos)Co(CS_2) [3]; a species which can be oxidized to **4** by the molecular oxygen in the air but is indefinitely stable under our reaction conditions; (iii) the known SO_2-metal complexes which react with O_2 generally form the corresponding SO_4 derivatives [9]. The known complex (triphos)Co(SO_4) [10] can be obtained by exposure of **5** to air.

Experimental

All preparations were carried out under an ultra-prepurified nitrogen.

Preparation of (triphos)Co(O_2CO) (3). Dry CO_2 was bubbled through solution **1** for two minutes. The solution immediately turned yellow, and the yellow complex began to separate. Addition of butanol and evaporation of the solvent completed the precipitation. The compound was filtered off, washed with butanol and petroleum ether, then dried in a stream of nitrogen. The complex was recrystallized from CH_2Cl_2/butanol to give green-yellow crystals (yield 40%).

The complexes (triphos)Co(S_2CO) (**4**) (yield 35%) and (triphos)Co(O_2SO) (**5**) (yield 40%) were prepared analogously. Analyses were in good agreement with the proposed formulae.

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