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Synthesis of the $Co_2(NO)_3^+$ Metallic Core Stabilized by Two Bridging Aminophosphines, with BPh_4^- as a Denitrosylating Reagent

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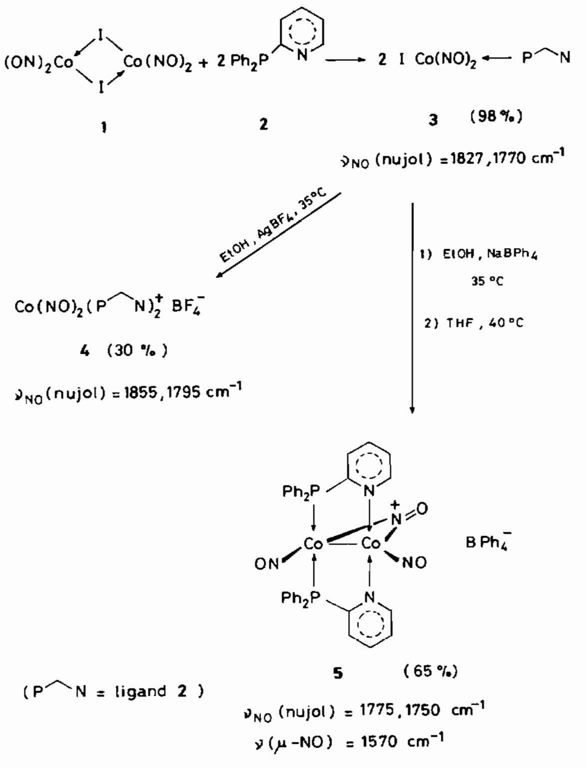
The tetraphenyl borate anion has been found to participate in a variety of reactions with transition metal complexes involving either the metal itself or one of the supporting ligands (see for example the references quoted in ref. 1). In this communication, we report that BPh_4^- can be used profitably with nitrosyl complexes for the generation of unusual metallic units.

Reaction of the iodobridged nitrosyl cobalt dimer (**1**) [2] with 2-pyridyldiphenylphosphine (**2**) [3] in ethanol at room temperature yields the monometallic complex **3** crystallizing out of the solution (see Scheme 1). Its X-ray crystal structure analysis [4] has shown that ligand **2** is P-bonded to the metal.



Scheme 1.

Halide removal from **3** with $AgBF_4$ in ethanol at 35 °C yields the new monometallic dinitrosyl cation **4** as the only complex isolated after removal of AgI, evaporation of the solvent to dryness and crystallization of the solid residue in CH_2Cl_2–toluene. As shown by an X-ray study [5], the two P/N ligands in **4** are P-bonded to the metal.

The course of the reaction is altered drastically when $NaBPh_4$ is used as the halide abstractor, under the same reaction conditions as before. A precipitate rapidly forms, and its dissolution in THF followed by a moderate heating at 40 °C affords ultimately a new crystalline product (after removal of THF and recrystallization in CH_2Cl_2–hexane). The presence of a vibration at 1570 cm^{-1} in its nujol IR spectrum was suggestive of a bridging NO, while the elemental analysis was consistent with the presence of one P/N ligand per cobalt. A crystallographic study of the compound undertaken to identify unequivocally its molecular structure has shown that it is complex **5** with the $Co_2(NO)_3^+$ metallic core stabilized by two bridging P/N ligands **2** coordinated in a head to head fashion [6], with a bridging nitrosyl ligand. A perspective view of the molecule is presented in Fig. 1 to illustrate the arrangement of the ligands around each metal. The structural study is at an intermediate stage of refinement due to problems with a disordered molecule of CH_2Cl_2 present in the unit cell. A detailed analysis of the structure will have to be deferred till these difficulties are resolved and also till the structure of $Co(NO)_2(pyridine)_2^+BF_4^-$ becomes available [7] to allow a more fruitful comparison with the structures of **4** and **5**. The Co...Co separation in **5** is 2.530(10) Å

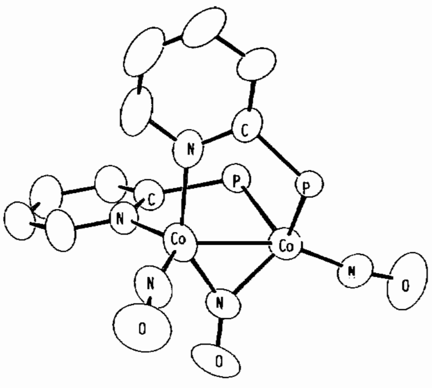


Fig. 1. Arrangement of the ligands around each cobalt in complex 5. BPh_4^-, the CH_2Cl_2 solvent and the P-phenyl substituents are omitted for clarity (triclinic; $P\bar{1}$; $a = 14.253$, $b = 15.489$, $c = 12.984$ Å; $\alpha = 95.62°$, $\beta = 91.35°$, $\gamma = 106.82°$).

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and it is not expected to change significantly upon further refinement. It is in agreement with the formulation of **5** containing a metal–metal bond.

Ligand **2** has been used extensively to construct bimetallic complexes of the second and third row elements frequently containing CO ligands (see for example ref. 8). To our knowledge however, complex **5** appears to be the first of its kind in which M–M bonded nitrosyl metallic fragments of a first row metal are connected to the P and N donor sites of 2.

Of much interest also is the formation of **5** with a NO/Co ratio of 1.5 from **3** where NO/Co = 2, thus implying the loss of a NO ligand. The BPh_4^- anion is most likely implicated in the denitrosylation step, and experiments are in progress to clarify the mode of removal of NO and to prepare other $(MM'(NO)_3)^{a+}$ ($a = 1, 0$) metallic cores with BPh_4^- as the denitrosylating reagent. Furthermore, complexes such as **5** should be well suited for reactivity studies aimed at the NO, the only reactive ligand present.

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