

New Cobalt(I) Complexes Derived from Dicarbonyltricyanocobaltate(I)

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Summary The preparation and characterization of several series of mixed ligand cobalt(I) complexes of the types $[\text{Co}(\text{CN})_2(\text{CO})_2(\text{PR}_3)]^-$, $[\text{Co}(\text{CN})_2(\text{CO})(\text{PR}_3)_2]^-$, and $[\text{Co}(\text{CN})(\text{CO})_2(\text{PR}_3)_2]$, prepared by the reactions of tertiary phosphines (PR_3) with $[\text{Co}(\text{CN})_3(\text{CO})_2]^{2-}$, are described and some novel aspects of their chemistry are discussed.

We have previously described the preparation of the cobalt(I) complex, $[\text{Co}(\text{CN})_3(\text{CO})_2]^{2-}$ (1), by the carbonylation of

aqueous solutions of either $[\text{Co}(\text{CN})_5]^{3-}$ or $[\text{Co}(\text{CN})_6\text{H}]^{3-}$ (refs. 1 and 2).

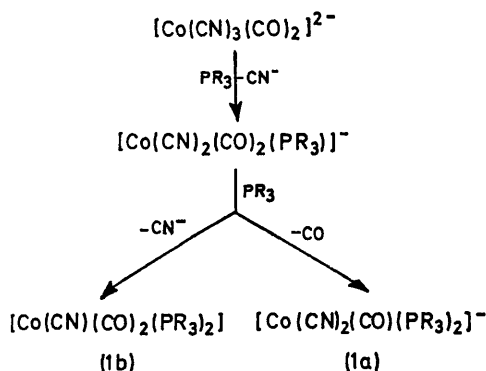
We now describe the preparation of several new series of mixed ligand cobalt(I) complexes of the types $[\text{Co}(\text{CN})_2(\text{CO})_2(\text{PR}_3)]^-$, $[\text{Co}(\text{CN})_2(\text{CO})(\text{PR}_3)_2]^-$, and $[\text{Co}(\text{CN})(\text{CO})_2(\text{PR}_3)_2]$ by reactions of tertiary phosphines (PR_3) with (1). Representative examples, together with their i.r. bands, are listed in the Table. Satisfactory elemental analyses were obtained for all these compounds.

TABLE

| Compound | $\nu_{\text{CN}}/\text{cm}^{-1}$ | $\nu_{\text{CO}}/\text{cm}^{-1}$ |
|--|----------------------------------|----------------------------------|
| $\text{Et}_3\text{N}[\text{Co}(\text{CN})_2(\text{CO})_2(\text{PCy}_3)] \cdot \text{H}_2\text{O}^{\text{a}}$ | 2105 m, 2085 ms | 1990 s, 1930 vs |
| $\text{Et}_3\text{N}[\text{Co}(\text{CN})_2(\text{CO})(\text{PPh}_3)_2] \cdot 2\text{H}_2\text{O}$ | 2081 m, 2065 ms | 1918 vs |
| $\text{K}[\text{Co}(\text{CN})_2(\text{CO})(\text{PMePh}_2)_2] \cdot 3\text{H}_2\text{O}$ | 2065 ms, 2050 m | 1890 vs |
| $\text{K}[\text{Co}(\text{CN})_2(\text{CO})(\text{PMe}_2\text{Ph})_2] \cdot 3\text{H}_2\text{O}$ | 2070 m, 2060 s | 1875 vs |
| $\text{K}[\text{Co}(\text{CN})_2(\text{CO})(\text{PEt}_3)_2] \cdot \text{CH}_3\text{COCH}_3 \cdot \text{H}_2\text{O}^{\text{b}}$ | 2062 m, 2045 ms | 1868 vs |
| $\text{K}[\text{Co}(\text{CN})_2(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)] \cdot \text{H}_2\text{O}$ | 2085 m, 2080 ms | 1905 vs |
| $[\text{Co}(\text{CN})(\text{CO})_2(\text{PPh}_3)_2]$ | 2100 m | 1988 s, 1932 vs |
| $[\text{Co}(\text{CN})(\text{CO})_2(\text{PEt}_3)_2]$ | 2095 m | 1968 s, 1905 vs |
| $[\text{Co}(\text{CN})(\text{CO})_2(\text{PCy}_3)_2]^{\text{a}}$ | 2092 m | 1967 s, 1908 vs |

^a Cy = cyclohexyl. ^b Recrystallized from acetone; formula confirmed by ¹H n.m.r.

Complexes of the type $[\text{Co}(\text{CN})_2(\text{CO})(\text{PR}_3)_2]^-$ were synthesized (in ca. 50% yields) by reaction of $[\text{Co}(\text{CN})_3(\text{CO})]^{2-}$ with the appropriate phosphine (2 mol. equiv.) under homogeneous conditions in aqueous methanol (1:1). The



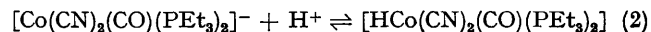
neutral bis-phosphine compounds of the type $[\text{Co}(\text{CN})(\text{CO})_2(\text{PR}_3)_2]$ were prepared heterogeneously by the addition of liquid phosphine or a solution in butanol of a solid phosphine to an aqueous solution of (1). Presumably $[\text{Co}(\text{CN})_2(\text{CO})(\text{PR}_3)_2]^-$ and $[\text{Co}(\text{CN})(\text{CO})_2(\text{PR}_3)_2]$ are derived from the common intermediate $[\text{Co}(\text{CN})_2(\text{CO})_2(\text{PR}_3)]^-$ (according to equation 1) through alternative paths involving the dissociation of CO or CN^- respectively, the latter being favoured by the two-phase reaction medium where CN^- is removed by the aqueous phase. The preparation of several complexes of this type, *i.e.* $[\text{Co}(\text{CN})(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{Co}(\text{CN})(\text{CO})_2(\text{PPhEt}_2)_2]$ by a different route, has recently been reported.³ In only one case, *i.e.* $[\text{Co}(\text{CN})_2(\text{CO})_2\{\text{P}(\text{cyclohexyl})_3\}]^-$, did we succeed in intercepting the reaction after the first substitution step and in isolating a pure salt of the monophosphine complex. Presumably steric factors oppose further substitution in this case although the corresponding bis(phosphino)-complex, $[\text{Co}(\text{CN})(\text{CO})_2\{\text{P}(\text{cyclohexyl})_3\}_2]$ could be obtained by reaction with additional $\text{P}(\text{cyclohexyl})_3$.

All the compounds were decomposed by oxygen; their reactivities ranged from pyrophoric for $\text{K}[\text{Co}(\text{CN})_2(\text{CO})(\text{PEt}_3)_2]$ and $\text{K}[\text{Co}(\text{CN})_2(\text{CO})(\text{PMe}_2\text{Ph})_2]$ to a slow decomposition for $\text{Et}_4\text{N}[\text{Co}(\text{CN})_2(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Co}(\text{CN})(\text{CO})_2(\text{PPh}_3)_2]$. Alkaline aqueous or alcoholic solutions of the

complexes are stable for several days in the absence of oxygen.

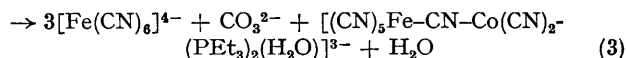
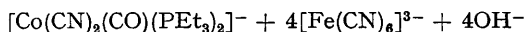
Our initial examination of the chemistry of these new complexes has revealed the following features.

(i) Lowering the pH of an aqueous solution of $[\text{Co}(\text{CN})_2(\text{CO})(\text{PEt}_3)_2]^-$ (λ_{max} 232 nm; ϵ 3.4×10^4) from 11 to 4 with HClO_4 results in a reversible spectral change and in the formation of a new species (λ_{max} 247 nm; ϵ 2.1×10^4), presumably the hydrido-complex $[\text{HCo}(\text{CN})_2(\text{CO})(\text{PEt}_3)_2]$, formed in accord with reaction (2) and having a $\text{p}K_a$ of ca. 5.



(ii) In contrast to certain other cobalt(I) complexes, *e.g.* $[\text{Co}(\text{dmg})_2(\text{PR}_3)]^-$,⁴ these complexes exhibit only weak nucleophilicity toward organic halides as reflected in the very slow reactions of $[\text{Co}(\text{CN})_2(\text{CO})(\text{PPh}_3)_2]^-$ and $[\text{Co}(\text{CN})_2(\text{CO})(\text{PEt}_3)_2]^-$ with benzyl bromide in methanol to yield rather unstable products which have not yet been characterized. The low nucleophilicities of these complexes, as well as their relatively low basicities toward protonation [equation (2)], presumably reflect the strong tendency of the CO ligand to stabilize cobalt(I) against oxidation.

(iii) $[\text{Fe}(\text{CN})_6]^{3-}$ reacts rapidly and quantitatively with $[\text{Co}(\text{CN})_2(\text{CO})(\text{PEt}_3)_2]^-$ in alkaline solution in the stoichiometric ratio 4:0:1. In accord with equation (3), one CO_3^{2-} ion is produced together with a dark orange compound (whose barium salt exhibits the characteristic i.r. bands of PEt_3 in addition to CN bands at 2125, 2065, and 2040 cm^{-1}) tentatively identified as $[(\text{CN})_5\text{Fe}-\text{CN}-\text{Co}(\text{CN})_2(\text{PEt}_3)_2(\text{OH}_2)]^{3-}$, *i.e.* the analogue of the ion $[(\text{CN})_5\text{Fe}-\text{CN}-\text{Co}(\text{CN})_5]^{6-}$ which is the product of the corresponding oxidation of $[\text{Co}(\text{CN})_5]^{4-}$ by $[\text{Fe}(\text{CN})_6]^{3-}$.⁵



The ready oxidation of the CO ligand in this reaction is of considerable novelty and interest. Further studies on this and other aspects of the chemistry of these new cobalt(I) complexes are in progress.

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