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Preliminary communication

Tautomerism in $[(R_3M)Co(CO)_3]_2$ complexes (R = alkyl, and M = P, As, or Sb); the consequences of changes in R and M

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Although the predominant species in solutions of $[(Et_3P)Co(CO)_3]_2$ does not contain bridging carbonyl groups, small amounts of CO bridged tautomers may be detected[1]. Replacement of the triethylphosphine by a triethylarsine ligand causes a marked increase in the importance of these bridged isomers[2]. The b—b and b—nb equilibria★ depend on solvent[2], and temperature[3].

The infrared spectrum of $[(Et_3Sb)Co(CO)_3]_2$★★ in heptane solution resembles that of its Et_3As analogue except that absorption bands due to the nb form are much weaker. Thus the b–$[(R_3M)Co(CO)_3]_2$ tautomers increase in importance for $R_3M = Et_3P < Et_3As < Et_3Sb$. A similar variation has been observed for complexes of the type $(R_3M)Co_2(CO)_7$ [4].

Both $[(n\text{-}Pr_3As)Co(CO)_3]_2$ and $[(n\text{-}Bu_3As)Co(CO)_3]_2$ show infrared spectra which are similar to that of the triethylarsine derivative. There are small changes in the b—b isomer ratio, but the proportions of nb species present in the solutions are more or less constant. However, both $[(i\text{-}Pr_3As)Co(CO)_3]_2$ and $[(i\text{-}Bu_3As)Co(CO)_3]_2$ exist largely or solely as nb tautomers of D_{3d} symmetry in heptane solutions. The dramatic consequences of the branching of alkyl groups in R_3M ligands is underlined by the absence of b complexes even in alkane solutions of $[(i\text{-}Pr_3Sb)Co(CO)_3]_2$.

The frequencies of the ν(CO) vibrations of these complexes do not vary markedly with the R_3M ligand. This suggests that the variations in isomer ratios are not due to electronic effects. Furthermore, the electronic consequences of substitution of a methyl group for a proton on the β-carbon atom would not be expected to be greatly different in going from $As(CH_2CH_2CH_3)_3$ to $As[CH_2CH(CH_3)_2]_3$ than from

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★ b = CO bridged isomer, and nb = non-bridged isomer.
★★ All new complexes were prepared as described in ref. 1, and were characterised by melting points, analyses, and infrared spectra.

$As(CH_2CH_3)_3$ to $As(CH_2CH_2CH_3)_3$.

A possible explanation for such changes may lie in the steric requirements of the R_3M ligand as the i-Pr and i-Bu groups, and thus i-Pr_3As and i-Bu_3As, are undoubtedly bulkier than their straight-chained homologues. Thus they would be expected to stabilize the nb isomers of D_{3d} symmetry where the interactions between R_3M and the other ligands would be much less important than the inter-ligand interactions in the b tautomers where the cobalt atoms are six, rather than five, coordinate[1,2]. This suggestion is consistent with the increase in importance of b–$[(R_3M)Co(CO)_3]_2$ species in going from $M = P < As < Sb$. The steric bulk of the R_3M ligand is due, primarily, to the three alkyl groups, R. The increase in the size of M along the above series serves to increase their separation from the cobalt atom, and thus to decrease the effective bulk of R_3M.

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