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# CATIONIC COMPLEXES OF COBALT(I) WITH PHOSPHINES AND CONJUGATED DIOLEFINS

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## Summary

The $\pi$-dienecobalt(I) derivatives $[Co(diene)(P)_3]^+$ (P = phosphine ligand) have been prepared by (1) reactions of conjugated dienes with $Co(ClO_4)_2 \cdot 6H_2O$ and phosphine and (2) by treatment of the $[CoH_2(P)_4]^+$ complexes with dienes.

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Oxidation of diene—dicarbonylcobalt dimers has been reported to yield diene—tricarbonylcobalt cations, or, in the presence of triphenylphosphine, the corresponding mono- or di-substituted complexes $[Co(diene)(CO)_{3-n}(PPh_3)_n]^+$ ($n = 1, 2$) [1]. We now find that trisubstituted $[Co(diene)(P)_3]^+$ complexes (P = secondary or tertiary phosphine) can be easily obtained by two simple methods.

Butadiene reacts in isopropyl alcohol with $Co(ClO_4)_2 \cdot 6H_2O$ (or other cobalt(II) salts containing non-coordinating anions) at room temperature in the presence of an excess of dimethylphenylphosphine, to give the yellow crystalline $[Co(butadiene)(PMe_2Ph)_3]ClO_4$. An analogous compound is obtained from the reaction involving isoprene. The complexes have been identified from analytical data (Table 1), chemical behaviour, and $^1H$ NMR spectra.

Gas chromatography of the thermal decomposition products of the complexes reveals the presence of the corresponding diene as a main component, confirming that there is $\pi$-coordination of the diolefin. Treatment of the $[Co(diene)(PMe_2Ph)_3]ClO_4$ complexes with CO causes displacement of the coordinated diolefin, with formation of the dicarbonyl derivative $[Co(CO)_2(PMe_2Ph)_3]ClO_4$ [$\nu$(CO) at 1950 and 2000 cm$^{-1}$]. The $^1H$ NMR spectrum of $[Co(butadiene)(PMe_2Ph)_3]ClO_4$ shows temperature and solvent dependence, and this will form the basis of a forthcoming publication. In $CH_2Cl_2$ solution at room temperature the methyl resonance of the phosphines appears as a broad signal centered at $\tau$8.50, while at —20°C two sharp

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES

| Compound | Colour | M.p. [a] (°C) | Analysis found (calcd) (%) |  |  | $\Lambda_M$ [b] (ohm$^{-1}$ cm$^2$ mol$^{-1}$) |
|---|---|---|---|---|---|---|
|  |  |  | C | H | P |  |
| $[Co(C_4H_6)(PMe_2Ph)_3]ClO_4$ | yellow | 146 | 53.23<br>(53.64) | 6.64<br>(6.27) | 14.71<br>(14.82) | 95 |
| $[Co(C_5H_8)(PMe_2Ph)_3]ClO_4$ | yellow | 121 | 53.50<br>(54.34) | 6.46<br>(6.45) | 14.63<br>(14.60) | 92 |
| $[CoH_2(HPPh_2)_4]ClO_4$ | pale-yellow | 106 | 64.58<br>(63.69) | 5.08<br>(5.12) | 13.80<br>(13.69) | — [c] |
| $[Co(C_4H_6)(HPPh_2)_3]ClO_4$ | yellow | 164 | 61.90<br>(62.31) | 5.17<br>(5.09) | 12.11<br>(12.05) | 98 |
| $[Co(C_5H_8)(HPPh_2)_3]ClO_4$ | yellow | 156 | 62.82<br>(62.72) | 5.28<br>(5.26) | 11.43<br>(11.83) | 93 |
| $[Co(C_6H_8)(HPPh_2)_3]ClO_4$ | yellow | 166 | 63.51<br>(63.28) | 5.05<br>(5.18) | 11.47<br>(11.64) | 92 |

[a] In sealed tube under vacuum. All compounds decompose explosively. [b] In nitromethane at 20°C for ca $10^{-3}$ *M* solutions. [c] Decomposes in dilute solution.

doublets are observed (ratio 2/1) at $\tau$8.72 [$J$(PH) = 4 Hz] and $\tau$7.98 [$J$(PH) = 7.5 Hz]. Similar solvent and temperature dependence is observed for the isoprene derivative.

The possibility of obtaining compounds of the type $[\mathrm{Co(diene)(P)_3}]^+$ by this method appears to depend on the nature of the phosphine. Thus, the reaction between butadiene and cobalt(II) perchlorate in isopropyl alcohol at room temperature and in the presence of methyldiphenyl- or triphenylphosphine does not yield any diene derivatives. In contrast, when diphenylphosphine is used, the complexes $[\mathrm{Co(diene)(HPPh_2)_3}]^+$ are slowly formed. This indicates that the size of the phosphine ligand is a controlling factor for the reaction.

Another simple method of isolating the cationic species $[\mathrm{Co(diene)(P)_3}]^+$ involves the treatment of the dihydrido derivatives $[\mathrm{CoH_2(P)_4}]^+$ (P = tertiary or secondary phosphine) with the appropriate diene. The procedure is illustrated by the following example.

The complex $[\mathrm{CoH(HPPh_2)_4}]$ [2] in ethanol suspension is treated with a stoichiometric amount of perchloric acid to give *cis*-$[\mathrm{CoH_2(HPPh_2)_4}]\mathrm{ClO_4}$ [$\nu$(CoH) at 1890 and 1925 cm$^{-1}$]. The dihydrido derivative is dissolved in tetrahydrofuran under argon, and addition of an excess of the requisite diene yields the complexes $[\mathrm{Co(diene)(HPPh_2)_3}]\mathrm{ClO_4}$. The cationic derivatives with butadiene, isoprene and 1,3-cyclohexadiene were conveniently prepared in this way (Table 1). Thermal decomposition and $^1$H NMR spectra confirm that the compounds contain one molecule of diolefin $\pi$-bonded to the cobalt. In $\mathrm{CH_2Cl_2}$, all three complexes react with CO at room temperature to give the dicarbonyl derivative $[\mathrm{Co(CO)_2(HPPh_2)_3}]^+$ [$\nu$(CO) at 1955 and 2005 cm$^{-1}$].

It is noteworthy that the dihydrido complexes $[\mathrm{CoH_2(L)(PR_3)_2}]^+$ (L = 2,2'-bipyridine, 1,10-phenanthroline) are known to undergo a rather similar reaction with butadiene, to form the cobalt(I) butadiene derivatives $[\mathrm{Co(diene)(L)(PR_3)}]^+$ [3].

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## References

1 F.M. Chaudhary and P.L. Pauson, J. Organometal. Chem., 69 (1974) C31.
2 A. Misono, Y. Uchida, T. Saito, M. Hidai and M. Araki, Inorg. Chem., 8 (1969) 168.
3 A. Camus, C. Cocevar and G. Mestroni, J. Organometal. Chem., 39 (1972) 355.