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Preliminary communication

DIENE—COBALT TRICARBONYL CATIONS

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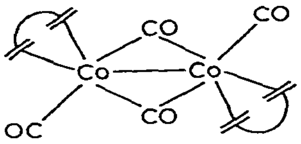
Summary

Oxidation of diene—dicarbonylcobalt dimers has yielded the novel diene—tricarbonylcobalt cations, or, in presence of phosphine, the corresponding mono- and di-substituted salts.

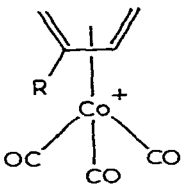
Many cationic metal carbonyls, isoelectronic with neutral complexes of the preceding metal in the periodic system, are known. Typical examples include the pairs $Mn(CO)_6^+$ and $Cr(CO)_6$; $C_7H_7Cr(CO)_3^+$ and $C_7H_7V(CO)_3$; $C_6H_6Mn(CO)_3^+$ and $C_6H_6Cr(CO)_3$; and $C_5H_5Fe(CO)_3^+$ and $C_5H_5Mn(CO)_3$. By analogy it should be possible to obtain salts of the type $(diene)Co(CO)_3{}^+X^-$ analogous to the well-studied diene—iron tricarbonyls. No general routes to such compounds have been described, although a methylcyclopentadienone(triphenylphosphine)dicarbonylcobalt cation [1] and some diene—cobalt cations with N and P donor ligands, e.g. $[C_4H_6Co(PBu_3)(o\text{-phen})]^+$ are known [2].

Two of the above cations are obtainable from $Mn(CO)_5X$ and $C_5H_5Fe(CO)_2X$ respectively by displacement of halide by carbon monoxide. But stable halides of the corresponding type $(diene)Co(CO)_2X$ are not obtained [3] from the dimeric diene complexes I, although cyclobutadienecobalt dicarbonyl halides are known [4,5]. We find however that direct oxidation of these dimeric complexes I yields the cation, e.g. IIa and b, and III, probably as a result of intramolecular transfer of a carbonyl group from one metal atom to another.

Triphenylmethyl hexafluorophosphate (or tetrafluoroborate) serves as an efficient electron abstractor for this oxidation, not only in the case of the butadiene and isoprene complexes, but even that of the cyclohexadiene complex; no evidence of hydride abstraction from the complex III so formed, or its neutral precursor of type I could be found. Alternative oxidising agents include ferric chloride, which reacts rapidly, and triethyloxonium tetrafluoroborate, which reacts slowly with the neutral complexes I. Appearance

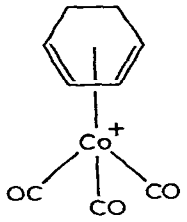


(I)

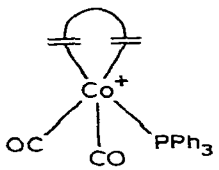


(II)

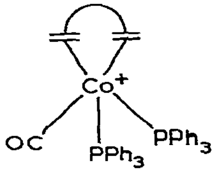
(a) R = H ; (b) R = Me



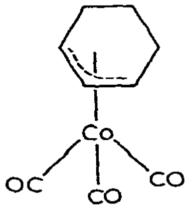
(III)



(IV)



(V)



(VI)

of new carbonyl stretching bands near 1845, 2035 and 2065 cm^{-1} suggests that formation of a cationic dimeric complex precedes rupture to yield the isolable salts II and III. Oxidations carried out in the presence of one mole of triphenylphosphine yield IV, the corresponding diene—triphenylphosphine-dicarbonylcobalt cations or, with excess of the phosphine give V, the diene—bis(triphenylphosphine)carbonylcobalt cations.

The cyclohexadiene complex (III) was also prepared by a second route: Addition of cobalt hydrocarbonyl, $HCo(CO)_4$, to 1,3-cyclohexadiene followed by hydride abstraction with triphenylmethyl hexafluorophosphate. Infrared examination indicated clearly the intermediate formation of the expected cyclohexenyl complex (VI) though this was not isolated.

Acknowledgement

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References

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