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Preliminary communication

BASIC METALS

IV*. THE SYNTHESIS OF MONOCYCLOPENTADIENYLCOBALT COMPLEXES CONTAINING Co—Zn, Co—Cu, Co—Sn AND Co—Hg BONDS

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Summary

The pronounced Lewis basic character of the metal atom in $C_5H_5Co(PMe_3)_2$ is demonstrated by its reactions with $ZnCl_2/PMe_3$, $[(PMe_3)_2CuCl]_2$, $SnCl_4$, R_3SnCl (R = Me, Ph) and $HgCl_2$ which lead to stable monocyclopentadienylcobalt complexes containing Co—Zn, Co—Cu, Co—Sn and Co—Hg bonds.

The concept of transition-metal basicity [2] has only rarely been applied to half-sandwich type complexes $C_mH_mML_n$ (L = PR_3, $P(OR)_3$, AsR_3 etc.). Monocyclopentadienyl-cobalt- and -rhodium-bis(phosphine) and -bis(phosphite) compounds have recently been prepared in our laboratories [1, 3] and thus allowed us to compare the reactivities of the compounds $C_5H_5M(CO)_2$, $C_5H_5M[P(OR)_3]_2$, and $C_5H_5M(PR_3)_2$ (M = Co, Rh) towards Lewis acids. The cobalt complex $C_5H_5Co(PMe_3)_2$ (I) [1] was by far to be the most reactive. On treatment with even weak acids HX, alkyl and acyl halides it forms the cations $[C_5H_5(PMe_3)_2CoH]^+$, $[C_5H_5(PMe_3)_2CoR]^+$ and $[C_5H_5(PMe_3)_2CoC(O)R]^+$, which contain unusually stable Co—H and Co—C bonds [1, 4].

We have now investigated reactions of I with metal halide compounds known to behave as Lewis acids. In an attempt to develop a one-step-synthesis of I starting from $CoCl_2$, C_5H_5Tl and excess PMe_3, and using metallic zinc as the reducing agent, we isolated, along with I, $[C_5H_5(PMe_3)_2CoZnCl_2(PMe_3)]$ (II). This complex has also been synthesized by the reaction of I with $ZnCl_2$ and PMe_3 in THF/ether.

Complex II reacts with water (in absence of air) to give the known cation

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[*] For Part III see ref. 1.

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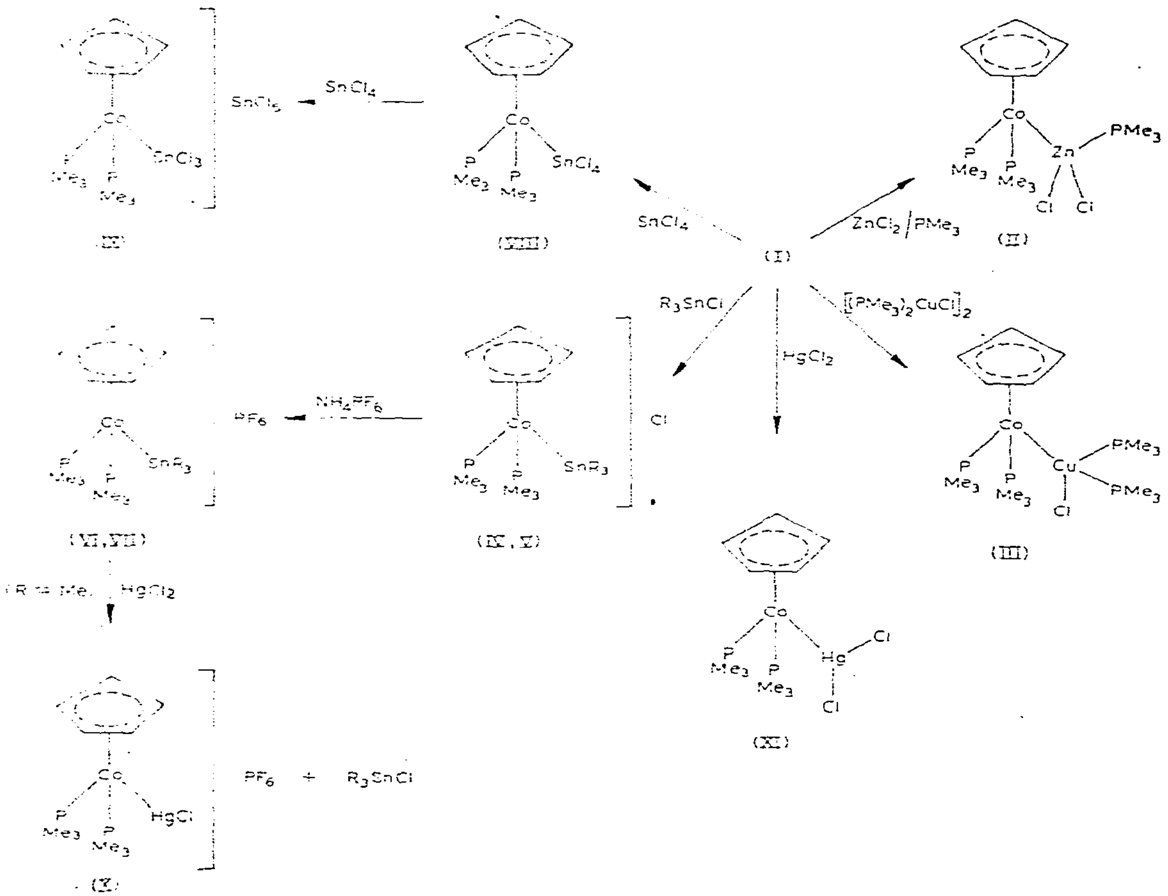
$[C_5H_5(PMe_3)_2CoH]^+$ [1], isolated as the PF_6 salt. The reaction of II with PMe_3 produces I and $(PMe_3)_2ZnCl_2$ in quantitative yields. Although NMR data for II could not be obtained because of the instability of its solutions, the complex was fully characterized by elemental analysis and its mass spectrum.

$[C_5H_5(PMe_3)_2CoCuCl(PMe_3)_2]$ (III) structurally analogous to II was prepared by treatment of I with $[(PMe_3)_2CuCl]_2$ [5] at 10°C in benzene. The NMR spectrum (in CD_3NO_2) shows the expected resonances for the cyclopentadienyl protons at δ 5.0 ppm and for the PMe_3 protons bonded to Co at δ 1.13 ppm and bonded to Cu at δ 0.87 ppm.

Reactions of I with R_3SnCl and $SnCl_4$ give two types of product. With R_3SnCl (R = Me, Ph), in ether at –70°C, oxidative addition occurs to give $[C_5H_5(PMe_3)_2\cdot CoSnR_3]Cl$ (IV, R = Me; V, R = Ph). Metathetical reactions of IV and V with NH_4PF_6 in methanol yield the corresponding hexafluorophosphate salts $[C_5H_5(PMe_3)_2CoSnR_3]PF_6$ (VI, R = Me; VII, R = Ph). Elemental analysis, NMR data (VI: δ (ppm, CD_3NO_2) 5.02 (C_5H_5), t, *J*(PH) 0.9 Hz; 1.5 (PMe_3), virt.t; 0.66 ($SnMe_3$), s (with satellites), *J*(SnH) 21.7 Hz; VII: δ (ppm) 5.40 (C_5H_5), t, *J*(PH)

SCHEME 1



1.0 Hz; 1.6 (PMe_3), virt.t; 7.5 (C_6H_5), m (60 MHz)) and conductivity measurements (VII: Λ_M 65.7 cm^2 mol^{-1} Ω^{-1}, in CH_3NO_2 at 25°C) are in accord with the proposed structure.

With $SnCl_4$, on the other hand, I reacts under the same conditions to form a 1/1 adduct $[C_5H_5(PMe_3)_2CoSnCl_4]$ (VIII). Further reaction of VIII with a second mol of $SnCl_4$ in acetone at −70°C gives the most interesting compound $[C_5H_5(PMe_3)_2CoSnCl_3][SnCl_5]$ (IX) which is one of the rare examples of stabilization of an organometallic cation by the $SnCl_5^-$ anion (^{1}H NMR of IX: δ (ppm in CD_3NO_2) 5.32 (C_5H_5), s; 1.44 (PMe_3), virt.t; Λ_M 89.3 cm^2 mol^{-1} Ω^{-1}, in CH_3NO_2 at 25°C). It should be noted that the dicarbonyl complex $C_5H_5Co(CO)_2$ reacts with SnX_4 (X = Cl, Br, I) at room temperature to yield $[C_5H_5(CO)CoSnX_3(X)]$ [6], but in this case, it was not possible to isolate the Lewis acid/Lewis base adduct $[C_5H_5(CO)_2CoSnCl_4]$ formed before the elimination of one mol of CO.

Mercuric dichloride preferentially cleaves the Co—Sn bond in VI to give, along with Me_3SnCl, the complex $[C_5H_5(PMe_3)_2CoHgCl]PF_6$ (X), in about 60% yield. With I, $HgCl_2$ reacts to give a 1/1 adduct (XI), which rapidly decomposes in solution and probably possesses a similar structure to that of $[C_5H_5(CO)_2CoHgCl_2]$ [7]. Scheme 1 summarises the results so far obtained on the reactions of $C_5H_5Co(PMe_3)_2$ (I) with Lewis-acidic metal halides. It clearly demonstrates the strong Lewis basic behaviour of the metal atom in the half-sandwich type complex I.

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