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Preliminary communication

APPROACHES TO ETHYL(PENTAMETHYLCYCLOPENTADIENYL)-RHODIUM OR -IRIDIUM COMPLEXES

AMELIO VÁZQUEZ DE MIGUEL and PETER M. MAITLIS*
Department of Chemistry, The University, Sheffield S3 7HF (Great Britain)

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Summary

Reaction of $[(C_5Me_5M)_2Cl_4]$ (M = Rh or Ir) with Al_2Et_6 gives $[C_5Me_5M(C_2H_4)_2]$ and some $[C_5Me_5MCl(\eta^3\text{-}CH_2CHCHMe)]$ but $[C_5Me_5RhEt_2(PMe_3)]$ is obtained from the reaction of $[C_5Me_5RhCl_2(PMe_3)]$ with Al_2Et_6.

We have recently reported on reactions of $[(C_5Me_5M)_2Cl_4]$ (Ia, M = Rh; Ib, M = Ir) with Al_2Me_6 to give a variety of novel complexes including $[C_5Me_5IrMe_4]$ [1], $[(C_5Me_5Rh)_2Me_2(\mu\text{-}CH_2)_2]$ [2], $[(C_5Me_5Ir)_2Me_2(\mu\text{-}CH_2)_2]$ [3] and $[(C_5Me_5Rh)_3(\mu_3\text{-}CH)_2]$ [4]. Most of these products resulted from unusual redox processes, at least one of which is now understood [2], on the first-formed species, $C_5Me_5MMe_2MeAlMeCl_6AlMe_2$. It was therefore of interest to compare these methylations with the reactions of Ia or Ib with Al_2Et_6.

Under conditions essentially identical to those used previously for reactions with Al_2Me_6, Ia reacted with Al_2Et_6 (molar ratio, 1/5) in benzene to give a dark brown solution. After work-up and chromatography on Florisil in hexane, the major product (31%) was identified as the known bis-ethylene complex $[C_5Me_5Rh(C_2H_4)_2]$ (IIa)* [5]. In addition a small amount (ca. 1%) of the η^3-1-methylallyl complex $[C_5Me_5RhCl(CH_2CHCHMe)]$ (IIIa) was also isolated. A number of variations involving different reagent ratios, solvents, temperatures and work-up procedures were tried but they gave the same products in similar amounts**.

Reaction of the iridium complex Ib with 3.6 equivalents of Al_2Et_6 in benzene

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*NMR spectra $[C_5Me_5Rh(C_2H_4)_2]$, ^{13}C ($CDCl_3$), δ 96.6 (C_5Me_5, d, J(Rh—C) 5.3 Hz), 43.8 (C_2H_4, d, J(Rh—C) 13.7 Hz) and 9.2 (C_5Me_5, s) ppm. $[C_5Me_5Ir(C_2H_4)_2]$, ^{13}C ($CDCl_3$), δ 92.5 (C_5Me_5), 24.1 (C_2H_4), and 8.8 (C_5Me_5) ppm.

**Attempts to detect ethyl-rhodium or -iridium complexes such as A (Scheme 1) by ^{13}C NMR spectroscopy at −90°C have not yet been successful. It appears that such species are unstable even under these conditions.

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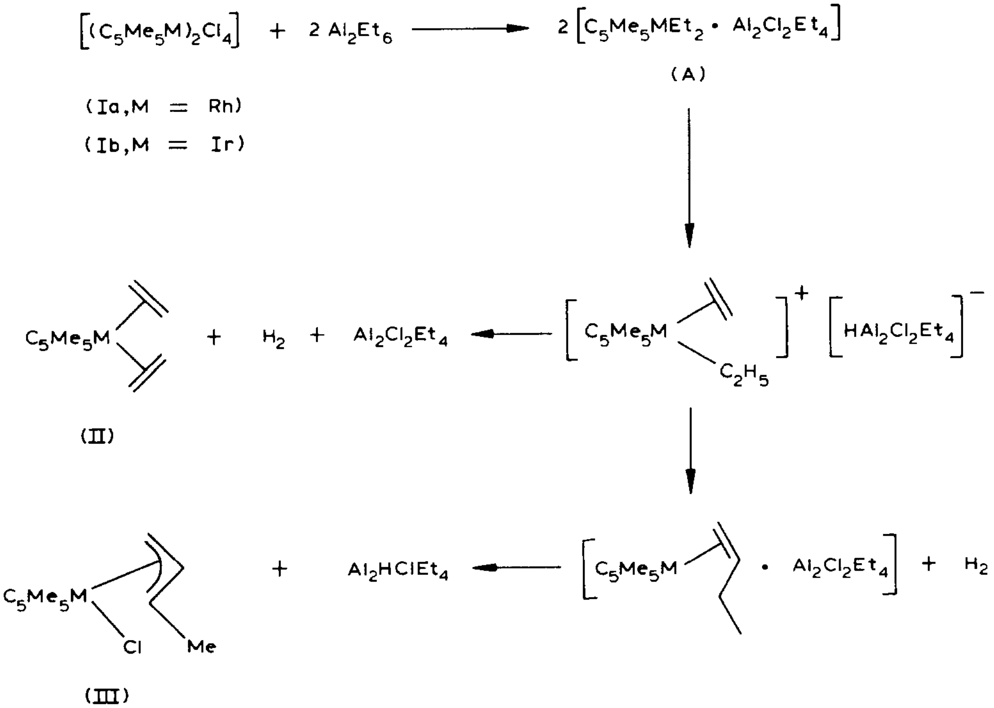
at 20°C proceeded similarly to give 21% of [$C_5Me_5Ir(C_2H_4)_2$] (IIb) and 2% of [$C_5Me_5IrCl(CH_2CHCHMe)$] (IIIb).

However, a diethylrhodium complex, the compound [$C_5Me_5RhEt_2(PMe_3)$] (IV) was obtained (24% after purification by chromatography) by reaction of [$C_5Me_5RhCl_2(PMe_3)$] with 1.4 equivalents of Al_2Et_6 in benzene. (Anal. Found: C, 54.6, H, 8.7, Mol. wt. (mass-spectroscopic) 372. [$C_5Me_5RhEt_2(PMe_3)$] calcd.: C, 54.8, H, 9.2%. Mol. wt. 372. ^{1}H NMR (220 MHz, C_6H_6), δ 1.91 (dd, PMe_3, J(P—H) = 8.2, J(Rh—H) = 0.7 Hz), 1.94 (m, RhCH_2), 2.61 (t, $\mathrm{RhCH_2}\mathit{CH}_3$, J(H—H) 7.3 Hz), 3.29 (d, $C_5\mathit{Me}_5$, J(P—H) 2.2 Hz) ppm. ^{13}C NMR (100 MHz, C_6D_6), δ 8.76 (m, Rh—$\mathit{C}H_2$), 9.79 (s, $C_5\mathit{Me}_5$), 14.86 (d, PMe_3, J(P—C) 27.5 Hz), 19.0 (s, Rh—$CH_2\mathit{C}H_3$) and 97.32 (dd, C_5Me_5, J(P—C) 2.3, J(Rh—C) 3.8 Hz) ppm.

Clearly the reason for the difficulty in isolating ethyl complexes or analogues of the μ_2-methylene or μ_3-methyne complexes from reaction of I and Al_2Et_6 is due to the high tendency of initially formed species such as A to undergo β-elimination in the absence of a strongly bonded ligand L. When a strong ligand such as trimethylphosphine is present then a diethylrhodium complex, for example IV, can be isolated. The routes leading to products II and III may be described as shown in Scheme 1.



SCHEME 1

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