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Preliminary communication

THE REACTION OF RUTHENIUM ATOMS WITH BUTA-1,3-DIENE: SYNTHESIS OF $[RuL(\eta^4\text{-}C_4H_6)_2]$ WHERE L = PF_3, CO AND $(CH_3)_3CNC$

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Summary

Condensation of ruthenium vapour with a mixture of pentane and buta-1,3-diene vapours at −196°C, followed by warming to −40°C, yields an unstable brown solution which reacts above −40°C with PF_3, CO or $(CH_3)_3CNC$ to give the corresponding complex $[RuL(\eta^4\text{-}C_4H_6)_2]$ in > 40% yield. The ease of isolation and purification of these air sensitive complexes decreases in the order $PF_3 > (CH_3)_3CNC > CO$.

Compounds of iron with buta-1,3-diene of type $[FeL(\eta^4\text{-}C_4H_6)_2]$ where L = CO or phosphines, are accessible by a variety of synthetic routes including chemical [1] or electrochemical [2] reduction and from iron atoms [3,4]. The only comparable ruthenium complex to be reported is $[Ru(PPh_3)(\eta^4\text{-}C_4H_6)_2]$, first made by Cole-Hamilton and Wilkinson from $[RuH_4(PRh_3)_3]$ and buta-1,3-diene at 100°C [5].

We have condensed ruthenium atoms with buta-1,3-diene at −196°C and, by addition of a ligand L to the cold condensate we have been able to isolate new complexes of type $[RuL(\eta^4\text{-}C_4H_6)_2]$. Typically, ruthenium vapour (70 mg, 0.69 mmol), evaporated under vacuum from a resistively heated tungsten wire [6] was condensed with a large excess of an equimolar mixture of pentane and buta-1,3-diene vapours on a surface cooled by liquid nitrogen. The condensate was warmed to −40°C, excess butadiene was pumped away and the remaining liquid filtered to give a clear brown pentane solution of the reaction products. Attempts to isolate organoruthenium compounds directly from this solution were not successful. However, allowing the brown solution to warm to room temperature in the presence of PF_3, CO or $(CH_3)_3CNC$,

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caused the solution to become yellow. No colour change was observed when the ligands were in contact with the solution at temperatures below −40°C. From the yellow solution obtained by reaction with PF_3, 90 mg (0.30 mmol, 43% yield) of air-sensitive, red-yellow crystals were obtained after crystallisation from pentane at −78°C (Anal.: Found: C, 32.24, H, 4.51. $C_8H_{12}F_3PRu$ calcd.: C, 32.33, H, 4.06%. NMR: ^1H δ 0.20 (ddd, 1 H) $J(H—P)$ 19.0 Hz, δ 1.70 (d, 1 H), 4.24 ppm (m, ^1H); ^{13}C-$\{^1H\}$ δ 35.27 (dq) ppm $J(C—P)$ 6.35, $J(C—F)$ 1.95 Hz, δ 78.4 (d) ppm $J(C—P)$ 3.40 Hz; ^{31}P-$\{^1H\}$ δ 172.5 (q) ppm $J(P—F)$ 1334 Hz; ^{19}F δ −2.91 (d) ppm. Mass spectrum, 70 eV (intensity for ^{102}Ru peaks): *m/z* 298 (16.2; M^+), 210 (100; $M - PF_3^+$), 156 (77.7; $RuC_4H_6^+$)). The ^1H NMR spectrum was not analysed in detail but it was clearly very similar to the $[AMX]_2$ pattern described for $[Ru(CO)_3(\eta^4\text{-}C_4H_6)]$ [7] with some additional coupling to phosphorus.

The isocyanide complex, purified in the same way as the PF_3 complex, appeared as an air-sensitive red-yellow oil, slightly contaminated with a polymer of $(CH_3)_3CNC$; this was evident from the ^1H NMR spectrum where there was a sharp singlet due to methyl protons of the polymer alongside the singlet due to the methyl protons of the coordinated ligand, and from chemical analysis for which C, H and N % values were always a little higher than required for $[Ru\{(CH_3)_3CNC\}(C_4H_6)]_2$ (^1H NMR, δ 0.28 (ddd, 4 H), 1.16 (s, 9 H), 1.92 (d, 4 H), 4.30 (t, 4 H) ppm. Mass spectrum: *m/z* 293 (25.3; M^+), 239 (19.8; $M - C_4H_6^+$), 210 {12.5; $Ru(C_4H_6)_2^+$}, 183 {100; $Ru(NC)(C_4H_6)^+$}, 156 (33.7; $RuC_4H_6^+$)). It was found possible to sublime small amounts of the complex at 60°C and 10^{-4} mbar pressure and a sample was purified for mass spectrometry in this way. No sublimation of the PF_3 or CO complex (see below) was observed under these conditions in contrast to the behaviour of the analogous iron compounds, although the ruthenium compounds gave satisfactory mass spectra using a heated probe unlet system.

The carbonyl complex, $[RuCO(\eta^4\text{-}C_4H_6)_2]$, proved even harder to purify than the isocyanide complex, and it was obtained only as an inseparable mixture of oil and crystals. The ^1H NMR spectrum was broad compared with that of the other complexes and additional features due to butadiene polymers were apparent. However, the mass spectrum was clean and showed the presence of the complex as the main volatile compound (mass spectrum: *m/z* 238 (17.0; M^+), 210 (99.4; $M - CO^+$), 156 (100, $RuC_4H_6^+$)). The infrared spectrum showed a strong $\nu(CO)$ bond at 2000 cm^{-1} whereas $\nu(CO)$ for $[Fe(CO)(\eta^4\text{-}C_4H_6)_2]$ [1] occurs at 1960 cm^{-1}.

We have also prepared the above compounds using electron bombardment evaporation of ruthenium, but noticed slightly greater contamination of the products by butadiene polymers.

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