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The Synthesis of (Chloro)η^3-2-chloromethylallyl(bisacetonitrile)dicarbonylmolybdenum(II)

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The complexes $[MCF_3CO_2(CO)_2L(\eta^3\text{-}C_3H_5)]$ (M = Mo and W; L = $CH_3O(CH_2)_2OCH_3$) have been found to act as catalysts for the polymerisation of certain dienes [1], and the halide phosphine substituted analogues have been utilised in organic synthesis for allylic alkylations [2–4]. Although a large number of these complexes have been made [5–14], hitherto none have been reported with a chloromethyl group attached to the allyl fragment which would tend to destabilise it. I wish, therefore, to report a two-step high yielding preparation of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$.

Experimental

$[Mo(CO)_6]$, $CH_2{=}C(CH_2Cl)_2$ and acetonitrile were purchased from commercial sources. The ^{1}H NMR spectrum was recorded on a Jeol FX60 NMR spectrometer. The infrared spectrum was recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analysis for carbon, hydrogen and nitrogen was recorded on a Carlo Erba Elemental Analyser MOD1106 (using a helium carrier gas).

Synthesis of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$

$[Mo(CO)_6]$ (4 g, 15.15 mmol) and 100 cm^3 of acetonitrile were refluxed under argon atmosphere for 24 h [15] in a 2 neck 250 cm^3 round bottomed flask, after which time the flask was cooled in an ice salt bath until the temperature reached –10 °C. A solution of (1.894 g, 15.15 mmol) of 3-chloro-2-chloromethylpropene in 10 cm^3 of acetonitrile was added dropwise with stirring over a period of 5 minutes. The reaction mixture was left for 2 h until carbon monoxide evolution had ceased, and the bright yellow solution, which after being reduced to half volume, cooled to –30 °C, afforded bright yellow crystals of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$. Yield 4.65 g, 85%. *Anal.* Calc. for $C_{10}H_{12}N_2O_2Cl_2Mo$: C, 33.43; H, 3.34; N, 7.80. Found: C, 33.20; H, 3.47; N, 7.96%. IR spectrum (nujol): ν(CN) = 2322 and 2291 cm^{-1}; ν(CO) = 1964 and 1878 cm^{-1}. At room temperature the ^{1}H NMR spectrum in $CDCl_3$ (calibrated against tetramethylsilane) showed resonances at δ = 1.19 (s, 2H, CH_α), 2.02 (s, 6H, NCMe), 3.58 (s, 2H, CH_β) and 3.8 (s, 2H, CH_2Cl).

Results and Discussion

Attempts to prepare $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$ by the most commonly used route for the synthesis of $[MoX(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4R\}]$ (R = H and Me) type compounds by refluxing $[Mo(CO)_6]$ in acetonitrile and 3-chloro-2-chloromethylpropene at 80 °C was unsuccessful and afforded only decomposition products. Reaction of $[Mo(CO)_3(NCMe)_3]$ [15] with 3-chloro-2-chloromethylpropene at –10 °C afforded high yields of the new yellow crystalline complex, $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$. The complex is both air and thermally sensitive, and is hence stored at 0 °C.

Microanalytical (C, H and N) data, infrared and ^{1}H NMR spectroscopy support the formulation of the new complex $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$ (see 'Experimental'). X-ray crystallographic studies on some analogous complexes containing bidentate nitrogen [16–19] ligands have shown that the geometry is essentially octahedral (assuming that the π-allyl group occupies one coordination site). The infrared and ^{1}H NMR data for the complex is consistent with this stereochemistry (Fig. 1). The allyl group is *trans-* to the chloride ion, the two *cis*-carbonyl groups are approximately co-planar with the acetonitrile ligands. The *cis*-carbonyl groups give two strong bands separated by 86 cm^{-1}.

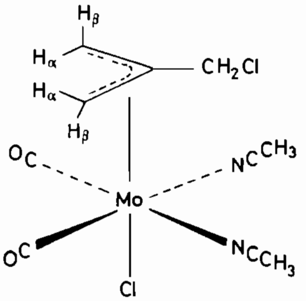

Fig. 1. Proposed structure of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$.

Attempts to synthesise the tungsten analogue was largely unsuccessful as even carrying out the addition of 3-chloro-2-chloromethylpropene with $[W(CO)_3\text{-}$

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$(NCMe)_3]$ at −30 °C decomposition of the allyl complex occurred very rapidly.

Preliminary studies of the reactions of $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$ indicate a facile displacement of the acetonitrile ligands in a similar manner to the methallyl complex $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_3)\}]$. For example, $[MoCl(CO)_2(NCMe)_2\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$ reacts at room temperature with an equimolar quantity of $Ph_2P(CH_2)_2PPh_2$ in CH_2Cl_2 to immediately afford the expected acetonitrile substituted product $[MoCl(CO)_2\{Ph_2P(CH_2)_2PPh_2\}\{\eta^3\text{-}C_3H_4(2\text{-}CH_2Cl)\}]$.

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