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RHENIUM(I) CARBONYL COMPLEXES DERIVED FROM TRIS(3,5-DIMETHYLPYRAZOLYL)BORATE ION *

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Summary

Treatment of $[Re(CO)_4Cl]_2$ with $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ giving $Re\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_3$ and $Re(3,5\text{-}Me_2C_3HN_2)_2(CO)_3Cl$, and bromination of the former to give $Re\{HB(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)_3\}(CO)_3$, without displacement of CO, is described.

Introduction

Although the η^5-cyclopentadienyl complexes of rhenium, $Re(\eta^5\text{-}C_5H_5)(CO)_3$ [1] and $Re(\eta^5\text{-}C_5H_5)(CO)_2Br_2$ [2] are well-known, the comparable tris(pyrazolyl)borato complexes are not. It has been shown [3] that there are strong similarities between the behaviour of metal complexes containing tris(pyrazolyl)borato anions, $[HB(C_3HR_2N_2)_3]^-$ (R = H or Me), and those containing the η^5-C_5H_5 ring. Thus, we would expect that rhenium carbonyl halides, by analogy with $Mn(CO)_5X$, [4], would react with $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ giving $Re\{HB(C_3HMe_2)_3\}(CO)_3$, and that this compound could be brominated giving $Re\{HB(C_3HMe_2N_2)_3\}(CO)_nBr_2$ (n = 1 or 2) in the same way that $M\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2$ is halogenated giving [5] $M\{HB(C_3HMe_2N_2)_3\}(NO)X_2$ (M = Mo or W; X = Cl, Br or I). Such rhenium halide complexes would be of interest because of the possibility that they might form stable monoalkylamido, hydrazido(1—) and alkoxy complexes analogous to the Mo and W nitrosyl species [6].

Results and discussion

Treatment of $[Re(CO)_4Cl]_2$ with $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ afforded two compounds, one the expected $Re\{HB(C_3HMe_2N_2)_3\}(CO)_3$ (I) and the other formulated as $Re(C_3HMe_2N_2)_2(CO)_3Cl$ (II). Compound I exhibited spectral characteristics entirely typical of a molecule of idealised C_{3v} symmetry, i.e. one BH and

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two CO stretching frequencies (KBr), and three signals in the ^{1}H NMR spectrum ($CDCl_3$) due to the two sets of methyl protons and to the protons at the 4-C position on the pyrazolyl rings. Compound II did not exhibit a BH stretching frequency, but an absorption at 3320 cm^{-1} was assigned to ν(NH), and, in contrast to I, three bands were detected in the range 2100—1800 cm^{-1}. The ^{1}H NMR spectrum of II exhibited four resonances, two due to the methyl groups, one due to the 4-protons in the pyrazolyl ring, and a broad singlet at low field which disappeared when solutions of II were treated with D_2O. This last signal is clearly due to an NH proton. Taking these data, and the elemental analyses into account, we must formulate II as a tricarbonylrhenium(I) species viz. $Re(3,5\text{-}Me_2C_3HN_2)_2(CO)_3Cl$. Since the $K[HB(C_3HMe_2)_3]$ used to prepare these compounds was pure, we can only surmise that some Re species in the reaction mixture is responsible for catalysing the decomposition of $[HB(C_3HMe_2N_2)_3]^-$ into pyrazole fragments.

Treatment of I with bromine in CCl_4 surprisingly did not lead to the formation of $Re\{HB(C_3HMe_2N_2)_3\}(CO)_2Br_2$. Although a reaction took place, giving a new white complex, III, the IR spectrum in the carbonyl region remained unchanged. From the ^{1}H NMR spectrum of the products, however, it was clear that substantial if not complete bromination of the 4-C atom in the pyrazolyl rings had occurred, since the signal appearing at δ 5.85 ppm in I had virtually disappeared. Also, while the IR spectra of I and III were virtually identical, an additional band appeared in the latter at 1108 cm^{-1} which may be attributed to ν(C—Br). Accordingly, we formulate III as $Re\{HB(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)_3\}(CO)_3$, notwithstanding the somewhat low Br analysis which, in part, may be accounted for by noting that bromination of I had not gone to completion and it proved almost impossible to separate small amounts of I from III. When bromination of I was carried out in CF_3CO_2H or benzene, a more nearly equal mixture of unreacted I and III was formed. This was established using the ^{1}H NMR spectra of the mixtures which showed two pairs of methyl proton resonances, two due to I at δ 2.33 and 2.45 ppm and two due to III at δ 2.36 and 2.48 ppm. The relative intensities of these two pairs of signals varied according to the precise reaction conditions, but we were never able to suppress one at the expense of the other in these solvents. Attempts to iodinate I were unsuccessful, only unchanged precursor being recovered from the reaction mixture.

These reactions are remarkable in that displacement of CO does not occur, but pyrazolyl ring halogenation is not without precedent. Thus chlorination of $Mo\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2$ afforded the simple dichloride and $Mo\{HB(3,5\text{-}Me_2\text{-}4\text{-}ClC_3N_2)_3\}(NO)Cl_2$ [5], and bromination of $W\{HB(C_3HMe_2N_2)_3\}(NO)(CO)_2$ afforded [6] $W\{HB(3,5\text{-}Me_2C_3HN_2)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)\}(NO)Br_2$ as the only readily characterisable bromination product.

Experimental

Rhenium carbonyl chloride, $[Re(CO)_4Cl]_2$ was prepared as described in the literature [7]. All reactions were carried out under nitrogen, and in N_2-degassed solvents. IR and ^{1}H NMR spectra were recorded using PE 180, Infrared 457 and PE R34 spectrometers, respectively. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

Re$\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_3$. To a solution of $[Re(CO)_4Cl]_2$ (0.67 g) in THF (40 cm^3) was added $K[HB(3,5\text{-}Me_2C_3HN_2)_3]$ (0.67 g), and the solution was stirred for 2 h. The mixture was then filtered and evaporated to dryness in vacuo. This oily residue was filtered out and washed with methanol (yield 0.35 g; 61%). IR spectrum (KBr): ν(BH) 2570, ν(CO) 2040, 1890 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 2.33 (singlet) and 2.45 (singlet) (total intensity 18; CH_3 of $[HB(C_3HMe_2N_2)_3]$), 5.85 ppm (singlet; intensity 1; 4-H of $[HB(C_3HMe_2N_2)_3]$). Analysis: Found: C, 38.16; H, 3.70; N, 14.38. $C_{17}H_{22}N_6O_3BRe$ calcd.: C, 38.09; H, 3.88; N, 14.81%. Mol. wt. (mass spectrum): calcd.: 568; found: 568.

Re$(3,5\text{-}Me_2C_3HN_2)_2(CO)_3Cl$. The methanol extract from above was evaporated to dryness, and the residue treated with fresh methanol. The white suspension of the desired compound was formed and was collected by filtration, washed with methanol and dried in vacuo (yields variable, but always less than 20%). IR spectrum (KBr): ν(NH) 3320, ν(CO 2050, 1930, 1890 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 2.22 (singlet) and 2.25 (singlet) (total intensity 6; CH_3 or $C_3HMe_2N_2H$), 5.91 (singlet; intensity 1; 4-H of $C_3HMe_2N_2H$), 10.89 ppm (broad singlet; intensity 1; NH). Analysis: Found: C, 30.90; H, 3.04; N, 11.25; Cl, 6.97. $C_{13}H_{16}N_4O_3ClRe_2$ calcd.: C, 31.13; H, 3.21; N, 11.25; Cl, 7.13%.

Bromination of Re$\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_3$*: Re*$\{HB(3,5\text{-}Me_2\text{-}4\text{-}BrC_3\text{-}N_2)_3\}(CO)_3$. To a suspension of $Re\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(CO)_3$ (0.28 g) in carbon tetrachloride (20 cm^3) was added a solution of bromine (0.16 g) in CCl_4 (5 cm^3), and the mixture was stirred for 3 h. During this time the solution changed from being colourless, to dark brown and eventually became yellow. The solvent was evaporated to dryness in vacuo, and THF was added to the residue affording a white solid. This was collected by filtration and the filtrate treated with n-pentane, which also gave a white solid. After several repetitions of this cycle, the white precipitates were combined and washed with n-pentane, giving the complex as a white solid (yield 0.26 g; 68%). IR spectrum (KBr): ν(BH) 2575, ν(CO) 2050, 1895 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 2.36 (singlet) and 2.48 (singlet) (CH_3 of $[HB(C_3BrMe_2N_2)_3]$. Analysis: Found: C, 27.23; H, 2.22; N, 9.73; Br, 24.27. $C_{17}H_{19}N_6O_3BBr_3Re$ calcd.: C, 26.87; H, 2.36; N, 10.45; Br, 29.82%.

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