Reactions of Chloroform and *gem*-Dichlorocarbons with Binuclear Rhodium Complexes leading to Functionalized Methylene-bridged Compounds

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Chloroform and *gem*-dichlorocarbons $CHCl_2R$ (R = H, Ph or CO_2Me) react rapidly with the binuclear basic metal complex $[\{Rh(\mu\text{-}pz)(CNBu^t)_2\}_2]$ (pz = pyrazolate) under a three-fragment four-electron scheme to give mainly the compounds $[\{Rh(\mu\text{-}pz)Cl(CNBu^t)_2\}_2(\mu\text{-}CHR)]$ (R = Cl, H, CO_2Me or Ph) and $[\{Rh(\mu\text{-}pz)Cl(CNBu^t)_2\}_2]$ as a side-product.

The oxidative addition of chlorocarbons to metal complexes is the initial step for their activation either by further transfer to organic molecules[1] or by their functionalization in possible catalytic processes.[2] Very electron-rich centres are required to produce rupture of the strong C–Cl bond, so that few reports on this type of reaction with dichloromethane[3] and chloroform[4] have appeared. Those involving mononuclear complexes lead to chloromethyl and dichloromethyl complexes through a two-electron two-fragment process.

We report here the easy three-fragment four-electron oxidative addition of chloroform and *gem*-dichloroalkanes to $[\{Rh(\mu\text{-}pz)(CNBu^t)_2\}_2]$ (pz = pyrazolate) to give functionalized methylene-bridged complexes. A precedent for this reaction does not exist either for chloroform (despite its thorough use as a deuteriated solvent in NMR spectroscopy) or for chloromethylene-bridged complexes; only the three-fragment four-electron oxidative addition of dichloromethane to the binuclear complexes $[Pd_2(dppm)_3]$ [dppm = bis(diphenylphosphino)methane][5] and $[\{Ru(\mu\text{-}Cl)(dppe)\}_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane][6] has been reported so far.[†]

The reported reactivity of rhodium pyrazolate carbonyl complexes is limited to ligand replacement reactions[8] and to their remarkably good catalytic activity for olefin hydroformylation under mild conditions.[9] Very few oxidative-addition reactions have been described for such compounds[10] in contrast with the extensive chemistry of their iridium counterparts.[11] To increase the basicity of the metal centres we have substituted formally the carbonyl groups by the isoelectronic and more strongly σ-donating alkyl isocyanide ligands. The compound $[\{Rh(\mu\text{-}pz)(CNBu^t)_2\}_2]$ **1** is prepared in good yield by replacement of cycloocta-1,5-diene (cod) in $[\{Rh(\mu\text{-}pz)(cod)\}_2]$ by Bu^tNC (molar ratio *ca.* 5:1, room temperature) in an inert solvent such as light petroleum. It is a yellow air-sensitive solid.[‡] A boat structure, with two bridging pyrazolate ligands, is indicated by the presence of three ν(CN) bands and the equivalence of the pyrazolate ligands and $CNBu^t$ groups in the ^1H NMR spectrum. This compound undergoes several kind of reactions (see Scheme 1). On the one hand, it can react as a double mononuclear complex. Thus methyl iodide reacts instantaneously with **1** in diethyl ether to give yellow crystals of the di-adduct $[\{Rh(\mu\text{-}pz)Me(I)(CNBu^t)_2\}_2]$ **2**. The addition at each metal centre is *trans* in such a way that the iodo ligands are in the pocket of the complex and the methyl groups outside according to nuclear Overhäuser enhancement (NOE) measurements.

Furthermore, complex **1** can undergo four-electron three-fragment reactions due to its high nucleophilic character and the close proximity of the metal centres. In this context,

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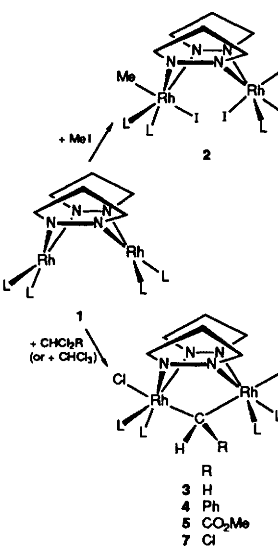
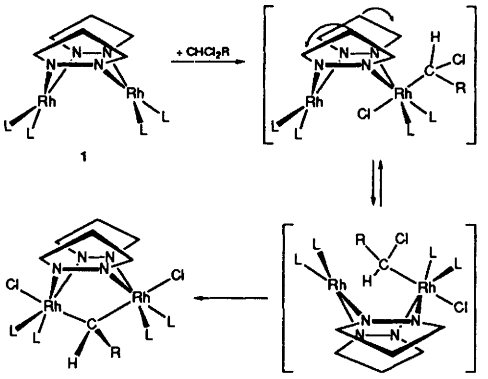
[†] Three-fragment two-electron oxidative addition of dichloromethane to mononuclear complexes has been observed where there is an additional basic centre in the ligand.[7]

[‡] Spectroscopic properties for the new compounds. **1**: IR (tetrahydrofuran) 2135s, 2100 (sh) and 2060s (CN) cm^{-1}; ^1H NMR (200 MHz, C_6H_6), δ 8.00 (d, 4 H, pz), 6.47 (t, 2 H, pz) and 0.92 (s, 36 H, $CNBu^t$). **2**: IR (CH_2Cl_2) 2215s and 2190s (CN) cm^{-1}; ^1H NMR ($CHCl_3$), δ 7.34 (d, 4 H, pz), 6.20 (t, 2 H, pz), 1.73 [d, $^2J(HRh)$ 2.1 Hz, 6 H, Me] and 1.57 (s, 36 H, $CNBu^t$). **3**: IR (CH_2Cl_2) 2215s, 2193s and 2166s (CN) cm^{-1}; NMR ($CHCl_3$), ^1H, δ 7.81 (d, 4 H, pz), 5.97 (t, 2 H, pz), 3.43 [t, $^2J(HRh)$ 1.4 Hz, 2 H, $\mu\text{-}CH_2$] and 1.46 (s, 36 H, $CNBu^t$); $^{13}C\text{-}\{^1H\}$ (50 MHz), δ 139.9 (pz), 135.0 [d, $^1J(CRh)$ 56, $\mathit{C}NBu^t$], 104.4 (pz), 58.8 ($CN\mathit{C}Me_3$), 31.1 ($CNC\mathit{Me}_3$) and 27.0 [t, $^1J(CRh)$ 22 Hz, $\mu\text{-}CH_2$]; fast atom bombardment (FAB) mass spectrum *m*/*z* 756 (M^+, 7) and 721 ($M^+ -$ Cl, 100%). **4**: IR (CH_2Cl_2) 2235s and 2195s (CN) cm^{-1}; NMR ($CHCl_3$), ^1H, δ 7.89 (d, 4 H, pz), 6.9 (m, 5 H, Ph), 6.19 (t, 1 H, pz), 6.11 (t, 1 H, pz), 5.56 [t, 1 H, $^2J(HRh)$ 2 Hz, $\mu\text{-}C\mathit{H}Ph$], 1.49 (s, 18 H, $CNBu^t$) and 1.20 (s, 18 H, $CNBu^t$); $^{13}C\text{-}\{^1H\}$, δ 162.0 (C_{ipso} Ph), 140.3 and 140.0 (pz), 135.4 [d, $^1J(CRh)$ 59, $\mathit{C}NBu^t$], 132.9 [d, $^1J(CRh)$ 55, $\mathit{C}NBu^t$], 128.2, 124.6 (Ph), 105.0 (pz), 58.8 ($CN\mathit{C}Me_3$), 58.2 ($CN\mathit{C}Me_3$), 52.4 [t, $^1J(CRh)$ 24 Hz, $\mu\text{-}\mathit{C}HPh$], 31.2 ($CNC\mathit{Me}_3$) and 30.5 ($CNC\mathit{Me}_3$). **5**: IR (CH_2Cl_2) 2223s and 2202s (CN) cm^{-1}; NMR ($CHCl_3$), ^1H, δ 7.84 (d, 2 H, pz), 7.78 (d, 2 H, pz), 6.09 (t, 1 H, pz), 6.07 (t, 1 H, pz), 4.18 [t, 1 H, $^2J(HRh)$ 2.2 Hz, $\mu\text{-}C\mathit{H}CO_2Me$] and 1.50 (s, 36 H, $CNBu^t$); $^{13}C\text{-}\{^1H\}$, δ 182.3 ($\mathit{C}O_2Me$), 140.2, 139.6, 104.8, 104.5 (pz), 59.0 ($CN\mathit{C}Me_3$), 58.8 ($CN\mathit{C}Me_3$), 50.9 ($CO_2\mathit{Me}$), 33.1 [t, $^1J(CRh)$ 24 Hz, $\mu\text{-}\mathit{C}HCO_2Me$], 31.0 ($CNC\mathit{Me}_3$) and 30.9 ($CNC\mathit{Me}_3$). **6**: IR ($CH_2Cl_2$) 2205s and 2175s (CN) cm^{-1}; NMR ($CHCl_3$), ^1H, δ 7.61 (d, 4 H, pz), 6.06 (t, 2 H, pz) and 1.49 (s, 36 H, $CNBu^t$); $^{13}C\text{-}\{^1H\}$, δ 138.8 [d, $^1J(CRh)$ 55 Hz, $\mathit{C}NBu^t$], 135.9, 105.2 (pz), 59.2 ($CN\mathit{C}Me_3$) and 31.6 ($CNC\mathit{Me}_3$). **7**: IR (CH_2Cl_2) 2226 and 2203s (CN) cm^{-1}; NMR ($CHCl_3$), ^1H, δ 7.85 (d, 2 H, pz), 7.74 (d, 2 H, pz), 6.46 [t, $^2J(HRh)$ 1.5 Hz, 1 H, $\mu\text{-}CHCl$], 6.10 (t, 1 H, pz), 6.03 (t, 1 H, pz), 1.50 (s, 18 H, $CNBu^t$) and 1.45 (s, 18 H, $CNBu^t$); $^{13}C\text{-}\{^1H\}$, δ 140.2 (pz), 133 [d, $^1J(CRh)$ ≈50, $\mathit{C}NBu^t$], 132 [d, $^1J(CRh)$ ≈50, $\mathit{C}NBu^t$], 105.1, 104.7 (pz), 66.2 [t, $^1J(CRh)$ 29 Hz, $\mu\text{-}CHCl$], 59.2 ($CN\mathit{C}Me_3$), 58.7 ($CN\mathit{C}Me_3$), 31.1 ($CNC\mathit{Me}_3$) and 30.6 ($CNC\mathit{Me}_3$); FAB mass spectrum *m*/*z* 757 ($M^+ -$ Cl, 18) and 672 ($M^+ -$ Cl $-$ $CNBu^t$, 100%).

All the new compounds gave correct elemental analyses.



Scheme 1 L = CNBu^t



Scheme 2 L = CNBu^t, R = H, Ph, CO_2Me or Cl

dichloromethane (5 cm^3) reacts cleanly and rapidly with **1** (0.5 mmol) affording a yellow solution of the methylene-bridged complex [{Rh(μ-pz)Cl(CNBu^t)$_2$}$_2$(μ-CH_2)] **3**. From this solution, complex **3** is isolated in 80% yield as pale yellow crystals, which are stable for long periods. A definitive proof of its structure comes from its ^1H and ^{13}C-{^1H} NMR spectra in which the bridging carbon and its protons appear as triplets due to their coupling with two equivalent ^{103}Rh nuclei. Other *gem*-dichloroalkanes, not containing β-hydrogen, such as dichloromethylbenzene and methyl dichloroethanoate react with **1** in a similar way giving the functionalized methylene-bridged complexes [{Rh(μ-pz)Cl(CNBu^t)$_2$}$_2$(μ-CHR)] (R = Ph **4** or CO_2Me **5**), in accord with their spectroscopic and analytical properties. Complexes **4** and **5** are isolated by crystallization in *ca.* 50 and 80% yield respectively. Abstraction of chlorine from the organic substrates to give the rhodium(II) complex [{Rh(μ-pz)Cl(CNBu^t)$_2$}$_2$] **6** occurs as a side-reaction to a small extent. The yield of this product in preparative reactions can be variable and is minimized by avoiding exposure to light and using carefully deoxygenated solvents. Complex **6** is the only isolated product, in low yield, when 1,1-dichloroethane, a *gem*-dichloroalkane containing β-hydrogen, is treated with **1**.

Chloroform, even in very dilute solutions, reacts rapidly with complex **1** in an inert solvent giving a yellow solution of the complex [{Rh(μ-pz)Cl(CNBu^t)$_2$}$_2$(μ-CHCl)] **7**. If this reaction is monitored by ^1H NMR spectroscopy in C_6D_6 it can be observed that complex **7** is formed in 95% yield in *ca.* 10 min with complex **6** as the only side-product. Complex **7** is isolated as yellow-orange crystals; its ^{13}C-{^1H} and ^1H NMR spectra show a triplet for the carbon and the proton respectively of the bridging chloromethylene group due to their couplings with two interacting rhodium nuclei.

No intermediates are observed in these reactions, which are completed in a few minutes at room temperature. When they are monitored by ^1H NMR spectroscopy, the starting material and the final products are the only species detected in the reaction medium. Most probably the halogenocarbon attacks one of the metal centres *via* the external face of the complex giving the corresponding oxidative-addition product. The addition should be *trans* as found in the reaction with methyl iodide (see Scheme 2). The flexibility of the Rh(pz)$_2$Rh six-membered ring allows an inversion of the boat configuration, which enables the halogenocarbyl group to approach the second metal centre where it undergoes a second oxidative-addition reaction. In this way, the CHR or CHCl fragments are incorporated as bridging ligands between the two metal centres.

Dichloromethane and chloroform are widely used as solvents in catalytic and NMR studies respectively although the latter is sometimes avoided because it is suspected that low-valent organometallic compounds may abstract chlorine from it. Nevertheless, we show here that both solvents and related chlorocarbons may react in a different way with binuclear complexes affording a simply entry to functionalized methylene-bridged compounds.

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