Some Unusual Hydrogen Shifts in Organo–Rhodium Complexes Formed from Diazoalkanes

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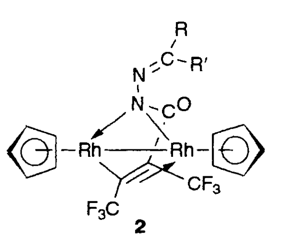
The products obtained from reactions of $Rh_2Cp_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ with the diazoalkanes N_2CMe_2 and $N_2C_5H_4$ include the compounds **3b** and **4** formed by N_2 elimination and 1,4- or 1,2-H shifts; the structure of compound **3b** has been determined by X-ray crystallography.

In the important field of metal mediated organic syntheses,[1] the transition metal rhodium[2] holds a special place. Over the past thirty years, it has been shown to assist an incredible variety of organic transformations; and yet, unexpected new reactions continue to emerge. In this communication, we describe some unprecedented H-shift reactions within organic ligands that are generated by adding certain diazoalkanes to the binuclear rhodium complex $Rh_2Cp_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ **1**[3] (Cp = cyclopentadienyl).



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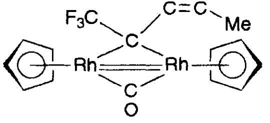
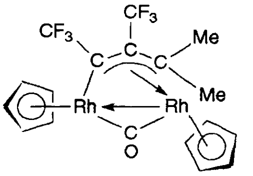
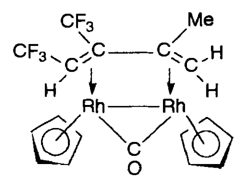


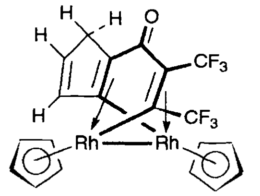
3a′



3a″



3b



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Treatment of **1** with N_2CMe_2 (diethyl ether, room temp., 5 min) gave two major products. From analytical and spectroscopic results, they are formulated as $Rh_2Cp_2\{\mu\text{-}C(CF_3)C(CF_3)C(O)NNCMe_2\}$ **2** (30% yield) and $Rh_2Cp_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3\cdot CMe_2)$ **3a** (20% yield). A complex analogous to **2** has been formed from **1** and N_2CMePh and the crystal structure of this complex was determined from X-ray diffraction data.[4] The structure shown for **2** is based on these results, and on similarities in the spectroscopic properties of **2**[†] and the N_2CMePh analogue.

[†] Satisfactory analytical data were obtained for each complex. *Selected spectroscopic data* for **2**: mass spectrum 596 (11%); IR (CH_2Cl_2) ν(CO) 1670 cm^{-1}; ^1H NMR ($CDCl_3$), δ 5.65 (d, 5H, J_{RhH} 0.9 Hz, C_5H_5), 5.25 (s, 5H, C_5H_5), 1.96 (s, 3H, CH_3), 1.74 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$), δ −47.8 (m, 3F, CF_3), −57.4 (q, 3F, J_{FF} 13 Hz, CF_3). For **3a**: mass spectrum 568 (5%), 538 (20%); IR (CH_2Cl_2) ν(CO) 1860 cm^{-1}; ^1H NMR ($CDCl_3$), δ 5.51 (d, 5H, J_{RhH} 0.7 Hz, C_5H_5), 5.32 (d, 5H, J_{RhH} 0.8 Hz, C_5H_5), 1.49 (s, 3H, CH_3), 1.19 (s, 3H, CH_3); ^{19}F NMR ($CDCl_3$), δ −53.6 (m, 3F, CF_3), −57.7 (m, 3F, CF_3). For **3b** mass spectrum 568 (5%), 538 (19%); IR (CH_2Cl_2), ν(CO) 1810 cm^{-1}; ^1H NMR ([$^2H_6$]acetone), δ 5.66 (s, 5H, C_5H_5), 5.61, (d, 5H, J_{RhH} 0.8 Hz, C_5H_5), 2.68 (t, 1H, $J_{HH} = J_{RhH} = 2.4$ Hz, CH_2), 2.24 (q, 3H, J_{FH} 2.4 Hz, CH_3), 0.95 [qm, 1H, J_{HF} 11.0 Hz, $CH(CF_3)$], 0.79 (t, 1H, $J_{HH} = J_{RhH}$ 2.4 Hz, CH_2); ^{19}F NMR ([$^2H_6$]acetone), δ −47.6 [m, 3F, $J_{HF} = J_{FF}$ 11 Hz and J_{RhF} 2.4 Hz, $C(H)CF_3$], −51.6 (m, 3F, CF_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ 128.0 (q, 1C, J_{FC} 274 Hz, CF_3), 91.0 (d, 5C, J_{RhC} 4 Hz, C_5H_5), 90.0 (d, 5C, J_{RhC} 4 Hz, C_5H_5), 38.0 (qd, 1C, J_{FC} 39 Hz and J_{RhC} 20 Hz, $CHCF_3$). For **4**: mass spectrum 590 (95%), 562 (8%); IR (CH_2Cl_2) ν(CO) 1690 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.09 (dt,1H, J_{HH} 5.2 and 2.0 Hz, C_5H_4), 6.17 (dt, 1H, J_{HH} 5.2 and 2.0 Hz, C_5H_4), 5.58 (s, 5H, C_5H_5), 5.09 (s, 5H, C_5H_5), 3.12 (dt, 1H, J_{HH} 22.8 and 2.0 Hz, C_5H_4), 2.49 (dm, 1H, J_{HH} 22.8 Hz, C_5H_4); ^{19}F NMR ($CDCl_3$) δ −52.3 (qd, 3F, J_{FF} 12 and J_{RhF} 2 Hz, CF_3), −55.4 (q, 3F,J_{FF} 12 Hz, CF_3); $^{13}C\{^1H\}$ ($CDCl_3$), δ 198.0 (br s, CO), 143.9 (s, CH), 135.6 (s, CH), 88.7 (d, $J_{RhC\text{-}5}$ Hz, C_5H_5), 88.3 (d, $J_{RhC\text{-}5}$ Hz, C_5H_5), 41.5 (s, CH_2).

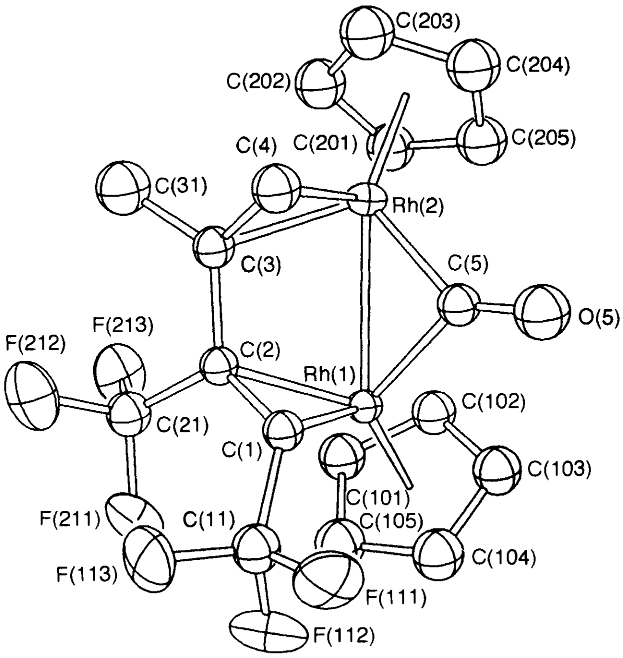

Fig. 1 Molecular structure of the complex **3**. Hydrogen atoms omitted. Important distances (Å): Rh(1)–Rh(2) 2.6846(4), Rh(1)–C(5) 2.027(4), Rh(1)–C(1) 2.096, Rh(1)–C(2) 2.115(5), Rh(2)–C(5) 1.954(5), Rh(2)–C(4) 2.132(6), Rh(2)–C(3) 2.182(5), C(1)–C(2) 1.439(6), C(2)–C(3) 1.500(6), C(3)–C(4) 1.427(6), C(5)–O(5) 1.179(6).

Spectroscopic results obtained for **3a**† indicate one of the structures shown, **3a′** or **3a″**. Each differs substantially from that established previously for a related complex $\mathrm{Rh_2Cp_2(CO)\{\mu\text{-}CF_3C_2CF_3{\cdot}C(H)CO_2Et\}}$.[5] In an attempt to confirm the molecular structure of **3a**, it was slowly recrystallized from toluene–hexane. Although good crystals were obtained, spectroscopic data† on the recrystallized product indicated that a remarkable 1,4-H shift had occurred during recrystallization. NMR results indicate that a hydrogen has migrated from one of the methyl groups in **3a** to a carbon with an attached trifluoromethyl group. This is confirmed by an X-ray diffraction study‡ on the recrystallized product **3b** (see Fig. 1). The ligand is now a butadiene group attached in an η^2,η^2-manner to the Rh–Rh bond.

The mode of formation of **3b** is unique. Although there are some other examples such as $\mathrm{Os_3(CO)_{10}(\mu\text{-}\eta^2,\eta^2\text{-}C_4H_6)}$[6] and $\mathrm{Co_2Cp_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}C_4H_6)}$[7] in which conjugated dienes are coordinated to a metal–metal bond, these complexes are obtained by direct addition of the butadiene to the appropriate Os_3 or Co_2 carbonyl precursor. It is of interest to note that additions of conjugated dienes to **1** do not yield products related to **3b**. Instead, there is H-transfer from the diene to the coordinated hexafluorobut-2-yne to form bis-alkenyl complexes of the type $\mathrm{Rh_2Cp_2\{\mu\text{-}\eta^1,\eta^2\text{-}C(CF_3){=}C(CF_3)H\}(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH\text{-}CH{=}CH_2)}$.[8] We are aware of one somewhat related example of a 1,4-H shift occurring in a binuclear complex. Thus, the 1,l-dimethylallene complex $\mathrm{NiMo(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}CMe_2{=}C{=}CH_2)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)}$ isomerizes on silica to form $\mathrm{NiMo(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}(\eta\text{-}C_5H_5)(\mu\text{-}C_5H_4Me)}$.[9]

From the reaction between **1** and the cyclic diazo compound $N_2C_5H_4$ (hexane, room temp., 30 min), a complex of formula $\mathrm{Rh_2Cp_2\{\mu\text{-}C_5H_4{\cdot}CO{\cdot}CF_3C_2CF_3\}}$ was obtained in 62% yield. The structure shown in **4** is derived from the spectroscopic data.† The presence of the cyclic 'ene–yne' unit (C_5H_4) within the bridging ligand is indicated by ^1H and ^{13}C NMR spectroscopy. Two alkene and the inequivalent methylene protons are revealed in the ^1H spectrum, and the ^1H–^1H coupling network is clearly disclosed in the COSY spectrum. Only three carbon signals are observed for this unit in the $^{13}C\{^1H\}$ spectrum, and this is consistent with two of the carbons having no attached protons. Two of the carbon resonances are in the alkene and the other in the alkane region: assignment of the CH=CH and CH_2 resonances was confirmed by the DEPT sequence. The carbonyl resonance in the ^{13}C spectrum was detected at δ 198. This is similar to δ(CO) for two other complexes known[10,11] to contain a $\mathrm{Rh_2(\mu\text{-}CO{\cdot}CF_3C_2CF_3)}$ unit. The presence of this group is also indicated by the typical ketonic absorption in the infrared spectrum and the high field shift of one CF_3 resonance in the ^{19}F NMR spectrum. The formation of this complex can be visualized in terms of the initial coordination of the cyclic carbene: C_5H_4, and a subsequent 1,2-H shift to produce a coordinated ene–yne ligand which undergoes a condensation reaction with the $CF_3C_2CF_3$ and CO ligands. Several complexes containing related bridging pentadienone ligands have been formed previously in reactions between **1** and alkynes,[12] but none have involved cyclic alkynes.

This study extends the incredible range of products obtained from reactions between the binuclear rhodium compound **1** and diazo-compounds, and emphasizes how sensitive such reactions are to changes in the nature of the substituents on the diazo carbon atom.

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‡ *Crystal data* for **3b**: $C_{18}H_{16}F_6ORh_2$; M = 568.1, triclinic, space group $P\bar{1}$, a = 12.313(2), b = 9.365(2), c = 8.758(2) Å, α = 112.16(1), β = 91.97(1), γ = 105.40(1)°, V = 891.4(3) Å^3, Z = 2, D_c = 2.12, D_m = 2.11 g cm^{-3}, $F(000)$ = 552, μMo = 18.9 cm^{-1}, Mo-Kα radiation, numeric absorption correction applied, R = 0.040 and R_w = 0.044 for 4252 unique reflections with $I > 3\sigma(I)$ collected in the ω scan mode with a symmetric scan range of (0.75 + 0.3tanθ)°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.