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A one-pot method to prepare the carbene complex $[Tp^{Me_2,Cl}RhCl_2(CHNiPr_2)]$ from $[Tp^{Me_2,Cl}Rh(CO)_2]$, $CHCl_3$, and $NHiPr_2$

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Abstract

The complex $[Tp^{Me_2,Cl}Rh(CO)_2]$ reacts with chloroform to give quantitatively the rhodium(III) complex $[Tp^{Me_2,Cl}RhCl(CHCl_2)(CO)]$ resulting from the oxidative addition of a C–Cl bond. Further reaction with diisopropylamine gives the aminocarbene complex $[Tp^{Me_2,Cl}RhCl_2(CHNiPr_2)]$, whose X-ray crystal structure has been solved. Addition of an excess of diisopropylamine to $[Tp^{Me_2,Cl}Rh(CO)_2]$ in chloroform provides directly $[Tp^{Me_2,Cl}RhCl_2(CHNiPr_2)]$.

Keywords: Carbene; Rhodium; Hydrotris(pyrazolyl)borate; C–Cl activation

1. Introduction

Carbene complexes take a growing importance not only in coordination chemistry in their own right, but also as precursors in homogeneous catalysis [1]. Many of them advantageously replace classical two electron donor ligands (i.e., phosphines, etc.) thereby allowing a fine tuning of electronic and steric properties of transition metal complexes and catalysts [2]. We report that $[Tp^{Me_2,Cl}Rh(CO)_2]$ (**1**), in which the $Tp^{Me_2,Cl}$ ligand is tris(3,5-dimethyl,4-chloropyrazolyl)borate [3], reacts with chloroform to produce the rhodium(III) complex $[Tp^{Me_2,Cl}RhCl(CHCl_2)(CO)]$ (**2**) and that subsequent addition of diisopropylamine affords the aminocarbene complex $[Tp^{Me_2,Cl}RhCl_2(CHNiPr_2)]$ (**3**). This sequence can be conducted in a one-pot fashion, a mixture of $CHCl_3$, $NHiPr_2$ and **1** yielding **3** directly.

2. Results and discussion

An initially fast reaction occurs between the dicarbonyl complex [4,5] **1** (ν_{CO} 2059, 1984 cm^{-1}) and chloroform as ascertained by a colour change from dark to light yellow and by infrared spectroscopy (ν_{CO} 2110 cm^{-1}). The reaction rate then slows down so that the reaction goes to completion in roughly 48 h. **1** is then quantitatively transformed in $[Tp^{Me_2,Cl}RhCl(CHCl_2)(CO)]$ (**2**). **2** exhibits ν_{CO} at 2110 cm^{-1}, a wavenumber consistent with a rhodium(III) complex [3]. Complex **2** was fully characterized by elemental analysis and NMR spectroscopy. The rhodium bound $CHCl_2$ group is characterized by a doublet in ^1H NMR at δ 7.55 ($^2J_{RhH} = 3.4$ Hz), and a low field ^{13}C NMR doublet at δ 63.6 ($^1J_{RhC} = 29$ Hz, $RhCHCl_2$). The ^1H NMR chemical shift compares well with those reported by Vrieze and co-workers [6] for $[RhCl_2(CHCl_2)$-(2,6-(C(H)=N*t*Bu)$_2C_5H_3N$)] ($RhCHCl_2$, δ 7.35, d, $^2J_{RhH} = 3.6$ Hz). **2** results from C–Cl oxidative addition on **1** as described in Scheme 1. Most probably this reaction proceeds through a SN2 type mechanism and not

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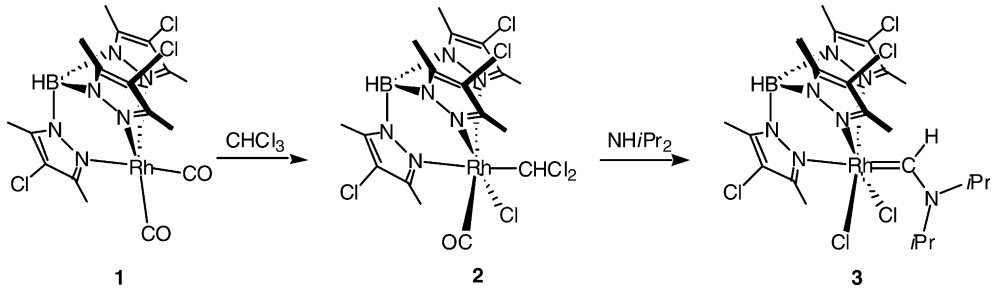

Scheme 1.

by a radical one. Indeed, $CHCl_3$ does not react with the pentacoordinated 18e species $[Tp^{Me_2}Rh(CO)_2]$, suggesting that the exclusive κ^3-mode of coordination of Tp^{Me_2} ligand prevents the reaction to occur [7].

Further reaction of **2** in chloroform with an excess of diisopropylamine (Scheme 1) produces a rhodium(III) complex which gave crystals of the diisopropylaminocarbene complex $[Tp^{Me_2,Cl}RhCl_2(CHNiPr_2)]$ (**3**) suitable for an X-ray analysis. The crystal structure of **3** (Fig. 1) reveals, apart from the $Tp^{Me_2,Cl}$ ligand bonded in its κ^3-mode, two chloro and a diisopropylaminocarbene ligand attached to a rhodium(III) metal centre. The overall orientation of the carbene ligand is in the molecular symmetry plane. The Rh–C(1) distance of 1.974(3) Å compares well with the rhodium–carbene distance in $[RhCl_3(CHNMe_2)(PEt_3)_2]$ which is 1.961(11) Å [8]. This bond is significantly shorter than that for a rhodium(I)–carbene (2.041(2) Å in [(COD)RhCl{C(N*i*Pr$_2$)$_2$}]) [9]. The Rh–N(5) bond length is significantly longer (2.135(3) Å) than the two other Rh–N(1) and Rh–N(3) distances (2.063(2), and 2.058(2) Å). This lengthening of 0.07 Å is indicative of the strong *trans* influence of the carbene ligand. The carbene-bound nitrogen N(11) is planar, and the carbon nitrogen C(1)–N(11) bond within the carbene (1.295(4) Å) shows some double bond character. It compares well with that (1.289(14) Å) in a dimethylaminocarbene $[RhCl_3(CHNMe_2)(PEt_3)_2]$ [8] and is somewhat longer that (1.147(5) Å) in an isonitrile complex $[Tp^{Me_2}RhCl(n\text{-}C_5H_{11})(CNCH_2CMe_3)]$ [10]. It is significantly shorter than the carbon-nitrogen single bonds observed in the N*i*Pr$_2$ group (1.490(4) Å and 1.508(4) Å) in **3**. Spectroscopically, **3** is characterized by a ^{1}H NMR doublet (RhC*H*N*i*Pr$_2$, δ 11.39, d, $^1J_{RhH} = 4$ Hz) and a ^{13}C NMR doublet (Rh*C*HN*i*Pr$_2$, δ 226.3, d, $^1J_{RhC} = 36$ Hz). A ν_{CN} band is observed at 1599 cm^{-1} in the infrared spectrum of **3**.

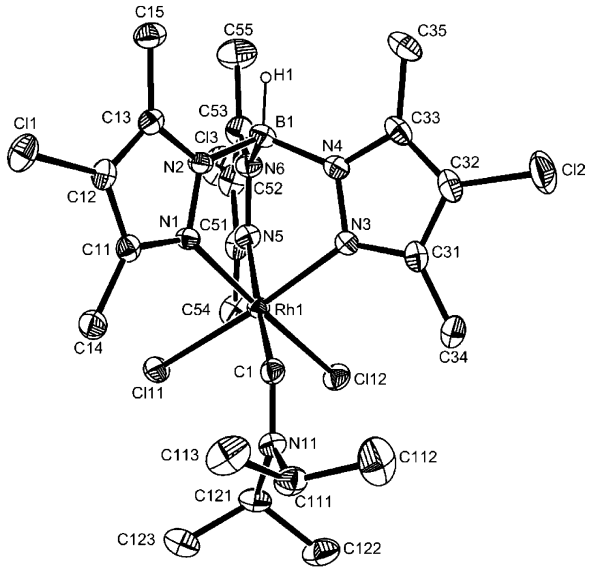

Fig. 1. Plot of the molecular structure of **3**. Salient bond lengths and angles: Rh(1)–C(1), 1.974(3), Rh(1)–N(1), 2.063(2), Rh(1)–N(3), 2.058(2), Rh(1)–N(5), 2.135(3), Rh(1)–Cl(11), 2.3430(6), Rh(1)–Cl(12), 2.3363(6), C(1)–N(11), 1.295(4) Å ; Rh(1)–C(1)–N(11), 135.85(16), Cl(11)–Rh(1)–Cl(12), 93.11(3), N(5)–Rh(1)–C(1), 175.13(7), Cl(11)–Rh(1)–C(1), 95.58(6), Cl(12)–Rh (1)–C(1), 92.82(6)°.

Preliminary attempts at understanding the reaction which transforms a dichloromethyl group in **2** into a (diisopropylamino)carbene ligand in **3** have been made. When the reaction between **2** and diisopropylamine was conducted in pentane, a white precipitate was identified as the ammonium chloride $[NH_2iPr_2]Cl$. This suggests that a dehydrochlorination process occurred, perhaps from an elusive intermediate such as $[Tp^{Me_2,Cl}Rh(CO)Cl(CHClN^+HiPr_2)]Cl^-$. This intermediate could rearrange first to $[Tp^{Me2,\ Cl}RhCl_2\ (CHClN^+HiPr_2)]^-$ with loss of CO then to **3** with loss of HCl trapped as $[NH_2iPr_2]Cl$. The iminium chloride $[iPr_2N{=}CHCl]Cl$ was also identified in solution ($\nu_{CN} = 1670$ cm^{-1})[8] during the reaction course. This is reminiscent of the synthesis of $[RhCl_3(CHNMe_2)\ (PEt_3)_2]$ from $[RhCl(CO)(PEt_3)]_2$ and $[Me_2N{=}CHCl]Cl$ [8]. In our hands, reacting $[iPr_2N{=}CHCl]Cl$ with **1** lead to decomposition of **1**. Thus, the main reaction course most probably involves the dehydrochlorination pathway. An alternative reaction course would be a Cl elimination from the $CHCl_2$ ligand of **2**, which would substitute the CO ligand and provide the $[Tp^{Me_2,Cl}RhCl_2(CHCl)]$ chlorocarbene species. Nucleophilic attack of the carbonic centre by the amine, as

already demonstrated in the literature [11], with loss of HCl, would give complex **3** [12]. Finally, addition of 20 equiv. of diisopropylamine to **1** in chloroform resulted in the formation of **3** directly, albeit in low yield (20%). Infrared monitoring of the reaction shows the intermediate formation of complex **2** consistent with oxidative addition of chloroform on **1** occurring first. Thus, the carbene complex **3** can be generated in a one-pot reaction from the readily available complex **1**.

Work is in progress to have more insight into this reaction in order to define its mechanism, and to explore its reactivity, especially in catalysis.

3. Experimental

3-1 Selected data for **2**: Anal. Calc. for $C_{17}H_{20}N_6BCl_6ORh$: C, 31.37; H, 3.10; N, 12.91. Found: C, 31.28; H, 3.06; N, 12.96%. ^{1}H NMR ($CDCl_3$): δ 2.29, 2.35, 2.36, 2.44, 2.69, 2.70 (s, 3H each, TpCH_3), 7.55 (d, $^2J_{RhH} = 3.4$ Hz, 1H, RhCHCl$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5, 11.1, 11.2, 11.5, 12.6, 13.9 (TpCH$_3$), 63.6 (d, $^1J_{RhC} = 29$ Hz, RhCHCl$_2$), 110.9, 111.2, 111.9 (TpC Cl), 141.6, 141.9, 143.0, 149.7, 149.9, 150.4 (TpCCH$_3$), 178.7 (d, $^1J_{RhC} = 61$ Hz, RhCO).

3-2 Selected data for **3**: ^{1}H NMR [CO(CD$_3$)$_2$]: δ 1.52, 1.61 (d, $^3J_{HH} = 6.7$ Hz, 6H each, CH(CH_3)$_2$), 2.19, 2.47, 2.48, 2.65 (s, 6:3:6:3H, TpCH_3), 4.63, 4.73 (hept, $^3J_{HH} = 6.7$ Hz, 1H each, CH(CH$_3$)$_2$), 11.39 (d, $^2J_{RhH} = 4.0$ Hz, 1H, Rh=CH). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 11.0, 11.5, 15.2, 15.7 (TpCH$_3$), 24.0, 24.4 (CH(CH$_3$)$_2$), 68.0, 68.5 (CH(CH$_3$)$_2$), 110.1, 110.2 (TpCCl), 141.8, 142.5, 149.6, 149.8 (TpCCH$_3$), 221.2 (d, $^1J_{RhC} = 36$ Hz, Rh=C).

3-3 Crystal data for **3**. $C_{22}H_{54}BCl_5N_7Rh$, monoclinic, $P2_1/n$, $T = 160(2)$ K, $a = 14.610(2)$, $b = 14.6626(16)$, $c = 14.722(2)$ Å, $\beta = 107.35(2)°$, $V = 3010.2(7)$ Å^3, $Z = 4$, reflections collected 29082/ unique 5913 ($R_{int} = 0.0358$), absorption corrections (semi-empirical), $T_{min} = 0.5034$, $T_{max} = 0.5953$, 339 parameters, full matrix least-squares refinement, $R_1 = 0.0305$, $wR_2 = 0.0715$ on F^2 (all data).

4. Supplementary material

The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition number: CCDC 230078. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] Recent review: W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290–1309.
[2] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39–91.
[3] S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligand, Imperial College Press, London, 1999.
[4] M. Paneque, S. Sirol, M. Trujillo, E. Carmona, E. Gutiérrez-Puebla, M.A. Monge, C. Ruiz, F. Malbosc, C. Leberre, P. Kalck, M. Etienne, J.C. Daran, Chem. Eur. J. 7 (2001) 3868–3879.
[5] Complex **1** presents an equilibrium involving the $Tp^{Me_2,Cl}$ ligand in a κ^2-bonding mode (ν_{CO}(KBr) = 2083 and 2017 cm^{-1}) and a κ^3-mode (ν_{CO}(KBr) = 2059 and 1985 cm^{-1}). F. Malbosc, V. Chauby, C. Serra-Le Berre, M. Etienne, J.-C. Daran, P. Kalck, Eur. J. Inorg. Chem. (2001) 2689–2697.
[6] H.F. Haarman, J.M. Ernsting, M. Kranenburg, H. Kooijman, N. Veldman, A.L. Spek, P.W.N.M. van Leeuwen, K. Vrieze, Organometallics 16 (1997) 887–900.
[7] M. Akita, K. Ohta, Y. Takahashi, S. Hikichi, Y. Moro-Oka, Organometallics 16 (1997) 4121–4128.
[8] B. Cetinkaya, M.F. Lappert, G.M. Laughlin, K. Turner, J. Chem. Soc., Dalton Trans. (1974) 1591–1599.
[9] K. Denk, P. Sirsch, W.A. Herrmann, J. Organomet. Chem. 649 (2002) 219–224.
[10] D.D. Wick, W.D. Jones, Organometallics 18 (1999) 495–505.
[11] P.J. Brothers, W.R. Roper, Chem. Rev. 88 (1988) 1293–1326.
[12] We thank one referee for suggesting this second mechanism.