DALTON COMMUNICATION

Diastereoselective C–H bond activation of diisopropylamine at a hydridotris(pyrazolyl)borato rhodium fragment

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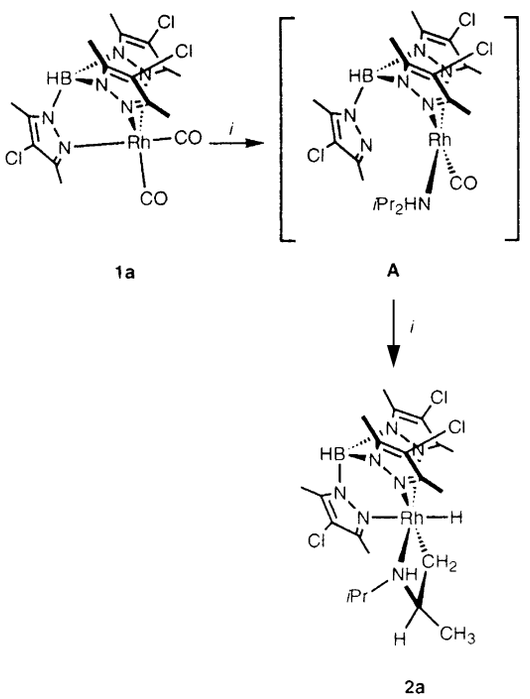
Irradiation of [$Tp^{Me2,Cl}Rh(CO)_2$] [$Tp^{Me2,Cl}$ = hydridotris-(4-chloro-3,5-dimethylpyrazolyl)borate] in diisopropyl-amine yields the C–H activated metallacycle [$Tp^{Me2,Cl}$RhH{$CH_2CH(CH_3)$NH*i*Pr}] as a single diastereomer.

In the last few years, significant progress has been made in the understanding of the mechanism by which late-transition metal complexes activate hydrocarbon C–H bonds.[1] In low valent systems, it is generally agreed that a coordinatively unsaturated metal centre coordinates an alkane to form a σ-complex[2] which then undergoes oxidative addition to yield an alkyl hydride complex. Hydridotris(pyrazolyl)borate (Tp′) complexes of rhodium efficiently intercept key intermediates during the photochemical C–H activation process.[3] As far as we are aware, the stereochemistry of the activation process has not been studied in detail. The outcome is however of potentially high importance if valuable chemicals are ultimately to be produced *via* such reactions. Optically active Tp′ ligands are available and some enantioselective reactions of their complexes have been described rendering an understanding of the stereochemistry of C–H activation an even more significant goal.[4] In this regard, it is interesting that an *intra*molecular diastereoselective C–H bond activation of a pendant isopropyl group has been reported in optically active [$Tp^{Menth}Rh(CO)_2$] [Tp^{Menth} = hydrotris[7(*R*)*i*Pr-4(*R*)Me-4,5,6,7-tetrahydroindazolyl]borate].[5] We report herein that complex [$Tp^{Me2,Cl}Rh(CO)_2$] (**1a**) [$Tp^{Me2,Cl}$ = hydridotris(4-chloro-3,5-dimethylpyrazolyl)borate] photochemically activates a primary C–H bond of diisopropylamine to give a *single* diastereomer of an hydrido rhodacycle.

Irradiation of a pentane solution of [$Tp^{Me2,Cl}Rh(CO)_2$] (**1a**) and excess diisopropylamine results in the formation of [$Tp^{Me2,Cl}$RhH{$CH_2CH(CH_3)$NH*i*Pr}] (**2a**) in 80% isolated yield (Scheme 1).† A faster and somewhat cleaner conversion (formation of by-products derived from C–H bond activation of pentane is prevented) is obtained in neat diisopropylamine. [$Tp^{Me2}Rh(CO)_2$] (**1b**) [Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)-borate] yields [Tp^{Me2}RhH{$CH_2CH(CH_3)$NH*i*Pr}] (**2b**)† only in the latter case.

The X-ray crystal structure‡ (Fig. 1) reveals **2a** to be an octahedral $Tp^{Me2,Cl}Rh(III)$ complex that contains a hydrido ligand, with the $CH_2CH(CH_3)$NH*i*Pr cycle tethered to rhodium *via* a single Rh–C bond and by amino coordination. The four atoms of the metallacycle are coplanar. The configuration of the stereogenic carbon C(17) and nitrogen N(7) is the result of minimised steric interactions. The isopropyl group on N(7) is *syn* to the $Tp^{Me2,Cl}$ ligand with an orientation directing this group in a wedge formed by two pyrazolyl rings. The unfavourable steric interaction with one pendant methyl group of $Tp^{Me2,Cl}$ [C(15) here] is thus alleviated. The methyl group on C(17) is *anti* to the vicinal isopropyl group and *syn* to the hydrido ligand. Should the configuration at C(17) be opposite, unfavourable interactions with both the isopropyl group and one pendant methyl group of $Tp^{Me2,Cl}$ [C(5) here] would be operative. Relevant spectroscopic data for **2a** follow. The hydrido ligand shows a ^1H NMR doublet at δ −16.90 ($^1J_{RhH}$ = 27 Hz) and a ν(Rh–H) at 2022 cm^{-1}. A ^{13}C NMR doublet at δ −11.0 ($^1J_{RhC}$ = 19 Hz) is assigned to the Rh-bound methylene carbon. 2-D NMR spectra have allowed the assignment of the two signals of the diastereotopic methylene hydrogen atoms (δ 1.56 and 2.03, unresolved multiplets).



Scheme 1 Reagents and conditions: *i* $NHiPr_2$, Ar purge, *hv*, −CO.

Reactivity studies on complex **2a** have met with little success so far. This may be attributed to the favourable octahedral coordination and the 18e count at Rh(III). We initially assumed that an available coordination site might be generated by the de-complexation of the amino nitrogen atom. CO (1 bar, 24 h, toluene, 60 °C) fails to coordinate and insert into the Rh–C bond. Under more forcing conditions (30 bar, 16 h, room temperature), very slow reductive elimination yields diisopropylamine and **1a** (*ca.* 15%). No evidence for C–D activation is obtained when **2a** is heated in C_6D_6 for 16 h. As expected, dichloromethane slowly reacts with **2a** to give [$Tp^{Me2,Cl}$RhCl{$CH_2CH(CH_3)$NH*i*Pr}] (**3**). ^1H, ^{13}C NMR, and NOESY experiments show that two diastereomers of **3** are present in solution: **3a** (*ca.* 75%) which has the same configur-

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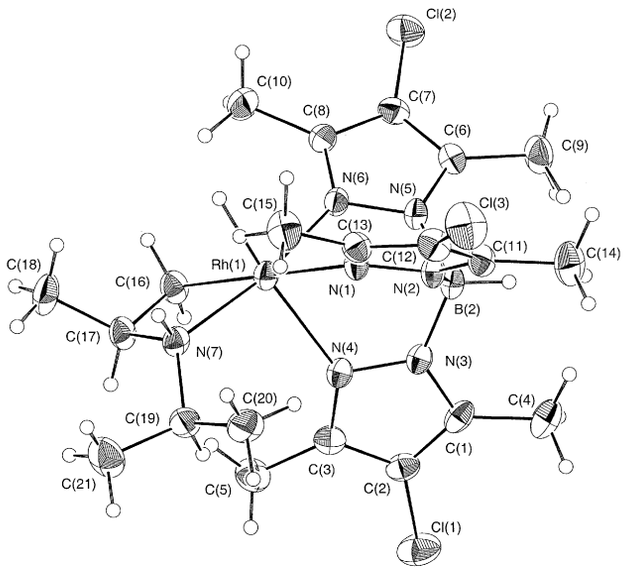

Fig. 1 Plot of the molecular structure of [$Tp^{Me2,Cl}$RhH{$CH_2CH(CH_3)$NH*i*Pr}] (**2a**). Relevant bond distances (Å) and angles (°): Rh(1)–N(1) 2.201(3), Rh(1)–N(4) 2.279(3), Rh(1)–N(6) 2.049(3), Rh(1)–N(7) 2.090(3), Rh(1)–C(16) 2.041(3); N(7)–Rh(1)–C(16) 69.7(2), Rh(1)–N(7)–C(17) 93.2(2), Rh(1)–C(16)–C(17) 95.2(2), N(7)–C(17)–C(16) 101.9(3).

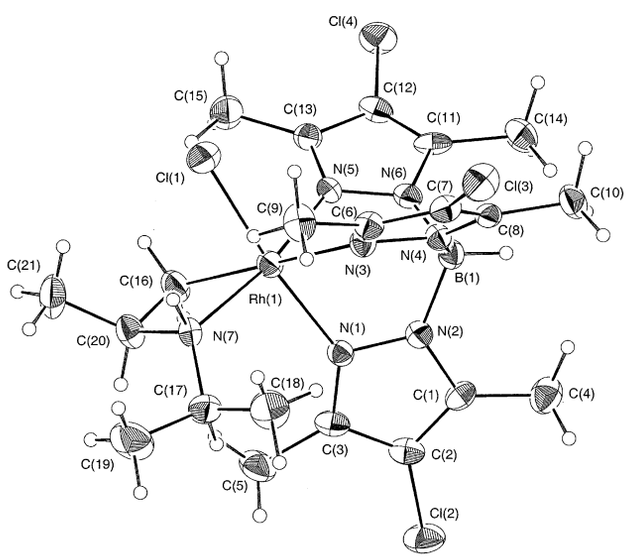

Fig. 2 Plot of the molecular structure of [$Tp^{Me2,Cl}$RhCl{$CH_2CH(CH_3)$NH*i*Pr}] (**3a**). Relevant bond distances (Å) and angles (°): Rh(1)–Cl(1) 2.340(2), Rh(1)–N(1) 2.112(5), Rh(1)–N(3) 2.238(4), Rh(1)–N(5) 2.078(4), Rh(1)–N(7) 2.100(4), Rh(1)–C(16) 2.057(5); N(7)–Rh(1)–C(16) 70.3(2), Rh(1)–C(16)–C(20) 94.7(3), Rh(1)–N(7)–C(20) 93.4(3), N(7)–C(20)–C(16) 101.6(4).

ation at carbon, nitrogen and rhodium as **2a**, and **3b** (*ca.* 25%) which differs in the configuration at rhodium. Chloroform reacts rapidly with **2a** to provide exclusively complex **3a**.† The X-ray crystal structure of **3a**‡ (Fig. 2) confirms the conclusions.

As ascertained by ^{1}H NMR spectra of crude reaction mixtures, the C–H activation reaction of diisopropylamime with **1a** proceeds diastereoselectively although three stereogenic centres (C, N and Rh) are generated. This is a rather unrecognised consequence of the use of Tp′ ligands in related C–H bond activation reactions. In addition to bands characteristic of complexes **1a** and **2a**, infrared spectra (KBr) recorded at different stages of the reaction show ν(CO) and ν(BH) stretches at 1971 and 2487 cm^{-1}, respectively. The latter is characteristic of a κ^2-Tp′ ligand[6] although the species is not stable enough to be identified by NMR techniques. We suggest that these two bands can be assigned to the somewhat electron-rich κ^2-$Tp^{Me2,Cl}$ diisopropylamine adduct [$Tp^{Me2,Cl}$Rh(CO)-($NHiPr_2$)] (**A**). In support of such a conclusion, the ν(CO) stretch of [κ^2-$Tp^{Me2,Cl}$Rh(CO)(PMe_3)] appears at 1963 cm^{-1}.[7] Following the recently reported preparation of [Bp^{Me2}-Rh(CO)(C_5H_5N)] [ν(CO) = 1972 cm^{-1}] [Bp^{Me2} = dihydridobis-(3,5-dimethylpyrazolyl)borate],[8] [κ^2-$Tp^{Me2,Cl}$Rh(CO)(C_5H_5N)] (**B**) was thermally generated from **1a**, pyridine and Me_3NO, in order to provide further evidence regarding the identity of **A**. Unfortunately **B** is not formed as cleanly as its Bp^{Me2} congener.[8] However, mass spectrometry (CI-NH_3, MH^+ = 612), infrared (ν(CO) and ν(BH) stretches at 1973 and 2482 cm^{-1}) and ^{1}H and ^{13}C NMR spectra (coordinated pyridine and six $Tp^{Me2,Cl}$ methyl signals) confirm its formulation. The subsequent C–H oxidative addition step in **A** requires elimination of the remaining CO ligand in order to accommodate the amine C–H bond. The diastereoselectivity, dictated by the topology of $Tp^{Me2,Cl}$, is undoubtedly expressed at this stage.

The outcome of thermal reactions is different in related systems. Double C–H activation of NMe_2Ph by [Tp^{Ph}Ir(η^4-isoprene)] [Tp^{Ph} = hydrotris(3-phenylpyrazolyl)borate] provides Fischer-type aminocarbene hydrido complexes.[9] Nucleophilic attack of primary amines on [$TpIr(CO)_2$] yields carbamoyl hydrido complexes.[10] The process we observe is reminiscent of the heteroatom (oxygen) assistance of C–H and C–F bond activations of pentafluoroanisole by a cyclopentadienyl rhodium complex.[11] However, diastereoselectivity is unique to our system.

Notes and references

† **2a** A mixture of **1a** (0.50 g, 0.89 mmol) and $NHiPr_2$ (2.50 mL, 17.9 mmol) in *n*-pentane was irradiated for four hours at 20 °C, while argon was bubbled through the solution. The mixture was then filtered and evaporated to give a yellow solid. Recrystallization from acetone at −20 °C afforded **2a** as yellow crystals (0.43 g, 0.71 mmol, 80%): ^{1}H NMR (400 MHz, C_6D_6): δ 4.28 (m, 1 H, CH_2CHCH_3), 2.66 (m, 1 H, CH_3CHCH_3), 2.57, 2.57, 2.38, 2.35, 2.25, 2.06 (all s, 3 H, CH_3 of $Tp^{Me2,Cl}$), 2.03, 1.56 (both m, 1 H, $RhCH_2$), 1.25 (d, $^3J_{HH}$ 6.5, 3 H, CH_2CHCH_3), 0.95 (m, 1 H, NH), 0.54, 0.40 (both d, $^3J_{HH}$ 6.2, 3 H, CH_3CHCH_3), −16.90 (d, 1 H, RhH, $^1J_{HRh}$ 27). ^{13}C{^{1}H} NMR (100 MHz): δ 148.84, 147.47, 146.72, 141.47, 140.58, 140.27 (CCH_3 of $Tp^{Me2,Cl}$), 109.44, 108.44, 108.13 (CCl of $Tp^{Me2,Cl}$), 72.53 (d, $^2J_{RhC}$ 5, $RhCH_2CH$), 53.73 (CH_3CHCH_3), 25.18 ($RhCH_2CHCH_3$), 22.24, 20.23 (CH_3CHCH_3), 14.00, 13.61, 12.95, 11.30, 10.89, 10.61 ($Tp^{Me2,Cl}CH_3$), −11.00 (d, $^1J_{RhC}$ 19 Hz, $RhCH_2$). IR (KBr, ν/cm^{-1}): 3267 (N–H), 2526 (B–H), 2022 (Rh–H). Found: C 43.52, H 6.03, N 14.79; $C_{21}H_{34}N_7BCl_3Rh{\cdot}CH_3COCH_3$ requires: C 43.50, H 6.08, N 14.79%.

2b ^{1}H NMR (250 MHz, C_6D_6): δ 5.87, 5.76, 5.44 (s, 1 H, CH of Tp^{Me2}), 4.38 (m, 1 H, CH_2CHCH_3), 3.53, 3.31 (m, 1H, $RhCH_2$), 2.76 (m, 1 H, CH_3CHCH_3), 2.49, 2.48, 2.41, 2.32, 2.30, 2.13 (s, 3 H, CH_3 of Tp^{Me2}), 1.29 (d, $^3J_{HH}$ 7, 3 H, $RhCH_2CHCH_3$), 0.57, 0.45 (both d, $^3J_{HH}$ 7, 3 H, CH_3CHCH_3), −16.55 (d, $^1J_{HRh}$ 27 Hz, 1 H, RhH). IR (KBr, ν/cm^{-1}): 2033 (Rh–H), 2518 (B–H).

3a ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (m, 1 H, CH_2CHCH_3), 3.46, 2.99 (both m, 1 H, $RhCH_2$), 2.69 (m, 1 H, CH_3CHCH_3), 2.57, 2.44, 2.43, 2.42, 2.39, 2.26 (all s, 3 H, CH_3 of $Tp^{Me2,Cl}$), 2.1 (m, 1 H, NH), 1.60 (d, $^3J_{HH}$ 6.5, 3 H, CH_2CHCH_3), 1.18, 0.69 (both d, $^3J_{HH}$ 6.5, 3 H, CH_3CHCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.18, 148.90, 148.16, 143.27, 140.81, 139.35 (CCH_3 of $Tp^{Me2,Cl}$), 110.30, 109.60, 109.20 (CCl of $Tp^{Me2,Cl}$), 73.80 (d, $^2J_{RhC}$ 4, $RhCH_2CH$), 53.96 (CH_3CHCH_3), 24.69 ($RhCH_2CHCH_3$), 22.20, 21.12 (CH_3CHCH_3), 13.79, 12.73, 11.85, 11.65, 10.75, 10.30 (CH_3 of $Tp^{Me2,Cl}$), −0.18 (d, $^1J_{RhC}$ 16 Hz, Rh CH_2). IR (KBr, ν/cm^{-1}): 3237 (N–H), 2553 (B–H). Found: C 41.10, H 5.59, N 13.84; $C_{21}H_{33}N_7BCl_4Rh{\cdot}CH_3COCH_3$ requires: C 41.35, H 5.64, N 14.06%.

‡ Crystal data for **2a**: $C_{24}H_{40}BCl_3N_7ORh$, M = 631.762, monoclinic, $P2_1/c$, a = 12.3405(3), b = 12.3544(4), c = 21.1247(7) Å, β = 99.838(2)°, U = 3173.3(2) Å^3, Z = 4, μ = 6.6 cm^{-1}, T = 298 K, reflections collected/unique/used: 14125/7213 (R_{int} = 0.021)/4971 [$I > 3\sigma(I)$], 334 parameters, R/R_w 0.040/0.040.

Crystal data for **3a**: $C_{24}H_{39}BCl_4N_7ORh$, M = 697.152, monoclinic, $P2_1/n$, a = 12.2538(3), b = 12.4285(5), c = 20.5888(6) Å, β = 94.547(2)°, U = 3125.7(2) Å^3, Z = 4, μ = 0.91 cm^{-1}, T = 298 K, reflections collected/unique/used: 11966/6069 (R_{int} = 0.090)/5000 [$I > 3\sigma(I)$], 344 parameters, R/R_w 0.062/0.083. CCDC reference numbers 161062 and 161063. See http://www.rsc.org/suppdata/dt/b1/b105327m/ for crystallographic data in CIF or other electronic format.

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