Reversible C–H activation of a P^{t}Bu^{i}Bu$_2$ ligand to reveal a masked 12 electron [Rh(PR$_3$)$_2$]$^+$ cation†

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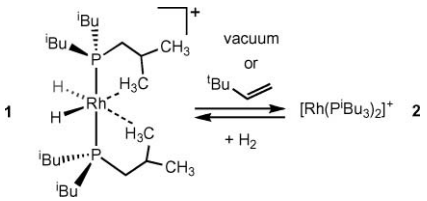
[Rh(P^t*Bu*^{i}Bu$_2$)$_2$][BAr$^F_4$], formed by removal of H$_2$ from [RhH$_2$(P^t*Bu*^{i}Bu$_2$)$_2$][BAr$^F_4$], is in rapid equilibrium between C–H activated Rh(III) isomers, but reacts as a masked 12-electron [Rh(P^t*Bu*^{i}Bu$_2$)$_2$]$^+$ Rh(I) cation.

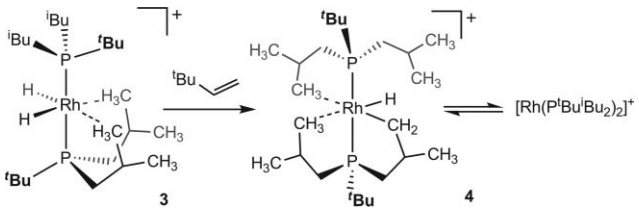
The generation and stabilisation of vacant sites on metal centres is a necessary requirement for many catalytic processes mediated by transition metals. In particular, the role of low-coordinate, low-valent, metal centres is central to many C–H and C–X activation processes.[1] We have recently reported on the synthesis of the formally 12-electron Rh(I) complex [Rh(P^{i}Bu$_3$)$_2$][BAr$^F_4$], **2**[2] [Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$], that undergoes oxidative addition reactions with aryl halides or H$_2$ and promotes dehydrocoupling of H$_3$B·NMe$_2$H *via* B–H activation.[3] Complex **2** is generated by removal of H$_2$ from [Rh(H)$_2$(P^{i}Bu$_3$)$_2$][BAr$^F_4$] **1**, a complex that itself is formally 14-electron and has two supporting C–H agostic interactions, Scheme 1. Although trapping experiments using ligands such as C$_6$H$_5$F and ClCH$_2$CH$_2$Cl indicate a Rh(I) formulation for **2** we have been unable to obtain a definitive structure of this important compound due to extensive disorder in the solid-state.



Scheme 1 Anions not shown.

Reasoning that changing the phosphine subtly might enforce a different packing regime in the solid-state we targeted the synthesis of the P^t*Bu*^{i}Bu$_2$ ligated complex: [Rh(P^t*Bu*^{i}Bu$_2$)$_2$][BAr$^F_4$], **4**. We find that in solution this complex is in rapid equilibrium between C–H activated Rh(III) isomers, but reacts as a masked[4] 12-electron [Rh(PR$_3$)$_2$]$^+$ Rh(I) cation (Scheme 2).

Addition of Na[BAr$^F_4$] to the new complex Rh(P^t*Bu*^{i}Bu$_2$)$_2$(H)$_2$Cl (see ESI†) in C$_6$H$_5$F solution affords [Rh(H)$_2$(P^t*Bu*^{i}Bu$_2$)$_2$][BAr$^F_4$], **3**, in good isolated yield (71%). In the solid-state compound **3** crystallises with two independent cations in the unit cell, both of which are disordered equally over crystallographically imposed inversion centres, and have similar structural metrics.



Scheme 2 Anions not shown.

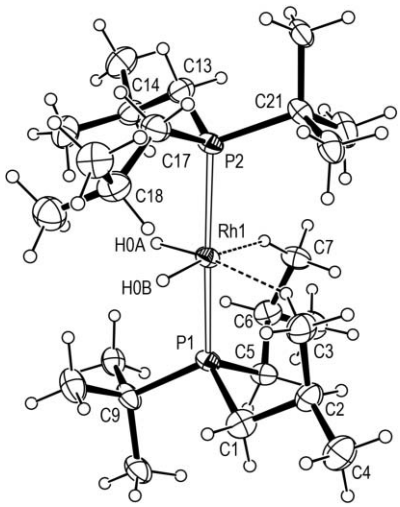


Fig. 1 Solid-state structure of one of the independent cations in the unit cell for **3**‡. Disordered components and [BAr$^F_4$]$^-$ anion are not shown. Thermal ellipsoids are given at the 30% probability level. Rh1–C7, 2.940(9) Å; Rh1–C3, 2.820(8) Å; Rh1–P1, 2.24(2) Å; Rh1–H0A, 1.457(11) Å; Rh1–H0B 1.448(11) Å; P1–C5–C6, 108.8(9)°; P1–C1–C2, 108.6(10) °; P2–C17–C18, 125.4(11)°; P2–C13–C14, 124.2(10)°.

Fig. 1 shows that they adopt a *trans* phosphine / *cis* dihydride arrangement of ligands which is completed by two agostic[5] C–H interactions from isobutyl groups on the same phosphine, making the cation approximately C$_s$ symmetric. This is different to the C$_2$-symmetric arrangement of the agostic interactions in **1**, although the Rh1···C bond distances, 2.940(9) and 2.820(8), are broadly similar [*viz*. 2.90(3), 2.891(5) Å in **1**]. Although rather weak interactions, these distances reflect their location relative to the high *trans* influence hydride ligands. They are, however, strong enough to manifest themselves in more compressed Rh1–P–C angles for the ^{i}Bu groups involved in agostic bonding, *cf.* P1–C1–C2, 108.6(10)° *versus* P2–C17–C18, 125.4(11)°.

In solution at 298 K the cation in **3** is fluxional and adopts time-averaged symmetry that makes the phosphine ligands equivalent, as evidenced by the observation of one phosphine, two diasterotopic ^{i}Bu-group, and one hydride environment [δ –22.03,

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J(RhH) 47 Hz, *J*(PH) 13 Hz]. On cooling to 190 K this pattern is retained, and no high-field signals due to agostic CH_3 groups were observed. This data suggests that rapid exchange on the NMR timescale is occurring between free and agostic CH_3 groups (as found for **1**[2]). On the IR timescale a broad stretch observed at 2671 cm^{-1} is assigned to the agostic CH_3 groups.[6] **3** is closely related to bis-phosphine and bis-*N*-heterocyclic carbene complexes of Rh(III) and Ir(III), as reported by Caulton[6] and Nolan[7] that show bis-agostic interactions.

Addition of *tert*-butylethene to **3** rapidly removes the hydrides to afford a new complex of empirical formula $[Rh(P^tBu^iBu_2)_2][BAr^F{}_4]$ **4** (51% isolated yield, quantitative by *in situ* NMR spectroscopy). Hydrogen loss is also promoted by vacuum, but this is much slower ($t_{\frac{1}{2}}$ ~15 h, 6×10^{-2} mbar). As for **3**, complex **4** crystallises with two independent cations in the unit cell, both of which are disordered equally over crystallographically imposed inversion centres. Fig. 2 shows the solid-state structure of one of these, that demonstrates ε-C–H activation of one of the ^{i}Bu groups to form a Rh(III)-metallacycle, Rh1–C3 2.151(15) Å.[8,9] Two relatively close Rh1 · · · C interactions from C7 and C15 (2.811(13) and 2.981(13) Å respectively) indicate supporting C–H agostic interactions (IR: 2684 cm^{-1}, vbr) similar to those observed in **3** and other Rh(III) and Ir(III) bis-agostic complexes.[2,6,7] The Rh(III) coordination environment is completed by a hydride (confirmed by NMR spectrocopy) which was not located, but placed *trans* to the agostic interaction from C7 on the basis of a gap in the coordination sphere. In solution, the room temperature ^{1}H and $^{31}P\{^1H\}$ NMR spectra show broad resonances. Cooling to 173 K reveals four, closely related species by the observation of: four hydride resonances grouped around δ –22 that show coupling to ^{103}Rh [*J*(RhH) ~ 54 Hz]; at least 4 broad peaks between δ 0.25 and –0.34 (6 H total), assigned to agostic CH_3 groups;[8] and four pairs of phosphine environments in the $^{31}P\{^1H\}$ NMR spectrum that show mutual *trans* ^{31}P–^{31}P coupling [*J*(PP) ~300 Hz] on a Rh(III) centre [*J*(RhP) ~115 Hz]. These low temperature data are consistent with the observed solid-state structure. We suggest that these isomers in solution differ in the position of C–H activation of the diastereomeric ^{i}Bu phosphine groups (*e.g.* C3, C4, see ESI for diagram†). The structure of **4** is in contrast to that suggested for **2**, in which no cyclometallation was indicated by NMR spectroscopy at low temperature. This facile cyclometallation[9] on incorporation of a bulky *tert*-butyl group is directly connected to Shaw's "*gem-tert-butyl*" effect,[10] as well as the influence that steric bulk of a phosphine has on the interaction of C–H bonds with metal centres.[6]

The room temperature NMR data for **4** suggest a fluxional process is occurring, and although a Rh(III) complex in the solid-state and at low temperature, it reacts with H_2, NCMe and $H_3B{\cdot}NMe_3$ as if a Rh(I) species: giving **3**, *trans*-$[Rh(NCMe)_2(P^tBu^iBu_2)_2][BAr^F{}_4]$ **5** and $[Rh(\eta^2\text{-}H_3B{\cdot}NMe_3)(P^tBu^iBu_2)_2][BAr^F{}_4]$ **6**[3] respectively (Scheme 3). This suggests the fluxional process is one that rapidly equilibrates Rh(I) with Rh(III)-cyclometallated species by reversible H–C(sp^3) bond cleavage. Others have previously observed such reactivity,[4,9,11] notably Caulton and co-workers who reported that the 12-electron Rh(I) complex, $[(^tBu_2PCH_2SiMe_2)_2N]Rh$, is in rapid equilibrium with a cyclometallated Rh(III) hydride. Unlike **2**, complex **4** does not promote C–X activation with aryl halides, which we suggest is due to the inability to form an intermediate Rh(I) η-complex prior to oxidative cleavage,[2] presumably due to steric constraints. Consistent with this **4** does not form a benzene adduct, whereas **2** does form complexes with arenes.[2]

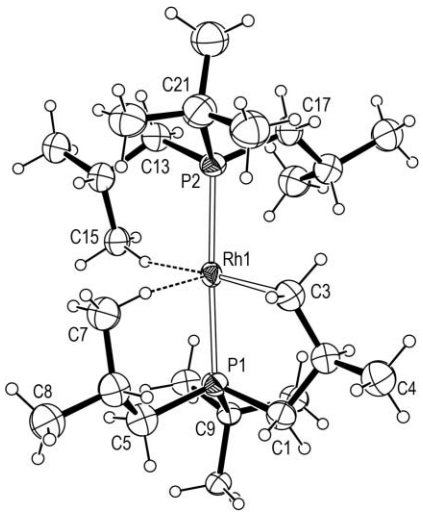
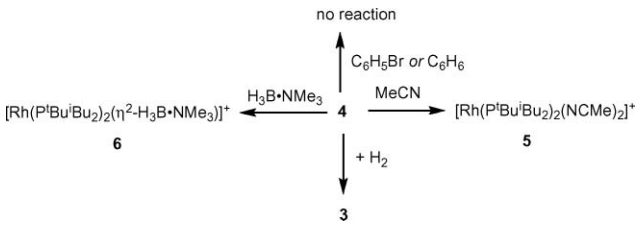


Fig. 2 Solid-state structure of one of the independent cations in the unit cell for **4**‡. Disordered components and $[BAr^F{}_4]^-$ anion are not shown. Thermal ellipsoids are given at the 30% probability level. The hydride ligand on Rh1 was not located (see text). Rh1–C3, 2.152(15) Å; Rh1–C7, 2.811(13) Å; Rh1–C15, 2.981(13) Å; Rh1–P1, 2.312(15) Å, Rh1–P2, 2.312(15) Å; P1–C1–C2, 106.9(12)°, P2–C13–C14, 116.3(11)°; P2–C17–C18, 117.3(10)°; P1–C5–C6, 116.1(11)°.



Scheme 3 Anions not shown.

Acknowledgements

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Notes and references

‡ Crystallographic data: **3**: $C_{56}H_{68}BF_{24}P_2Rh$, M = 1372.76, Triclinic, $P\bar{1}$ (Z = 2), a = 12.88050(10) Å, b = 13.05280(10) Å, c = 22.3154(2) Å, α = 103.1981(3)° , β = 94.4213(4)°, γ = 118.4125(4)°, V = 3136.24(4) Å^3, T = 150(2) K, 26387 unique reflections [R_{int} = 0.0193]. Final R_1 = 0.0560 [$I > 2\sigma(I)$]. **4**: $C_{56}H_{66}BF_{24}P_2Rh$, M = 1370.75, Triclinic, $P\bar{1}$(Z = 2), a = 12.9373(2) Å, b = 13.0919(2) Å, c = 22.2056(3) Å, α = 72.9625(7)°, β = 85.6901(6)°, γ = 60.4717(6)°, V = 3118.05(8), T = 150(2) K, 22967 unique reflections [R_{int} = 0.0252]. Final R_1 = 0.0722 [$I > 2\sigma(I)$]. **Selected NMR data (CD_2Cl_2; 298 K; ^{1}H, 500 MHz; $^{31}P\{^1H\}$, 202 MHz): Compound 3**: **^{1}H:** δ 7.72 (br, 8H, $BAr^F{}_4$), 7.56 (br, 4H, $BAr^F{}_4$), 1.95–1.79 (m, 8H, ^{i}Bu{CH/CH_2}), 1.73–1.67 (m, 4H, ^{i}Bu{CH_2}), 1.16 (apparent t, 18H, J = 7, ^{i}Bu{Me}), 0.89 (d, 12H, $^3J_{HH}$ = 6.5, ^{i}Bu{Me}), 0.81 (d, 12H, $^3J_{HH}$ = 6.5, ^{i}Bu{Me}), –22.03 (dt, 2H, $^1J_{RhH}$ = 47.1, $^2J_{PH}$ = 13.3, RhH). **Selected ^{1}H{^{31}P@56.9 ppm}:** δ –22.03 (d, 2H, J_{RhH} = 47.3, RhH). **$^{31}P\{^1H\}$:** δ 56.9 (d, $^1J_{RhP}$ = 109).**^{1}H (190 K):** δ 7.71 (br, 8H, $BAr^F{}_4$), 7.53 (br, 4H, $BAr^F{}_4$), 1.76 (br, 8H, ^{i}Bu{CH_2}), 1.54 (br, 4H, ^{i}Bu{CH}), 1.04 (br, 18H, ^{i}Bu{Me}), 0.75 (d, $^3J_{HH}$ = 4.6, 12H, ^{i}Bu{Me}), 0.67 (d, $^3J_{HH}$ = 4.2, 12H, ^{i}Bu{Me}), –21.48 (dt (br), $^1J_{RhH}$ = 44.9, $^2J_{PH}$ = 11.7, 2H, RhH). **$^{31}P\{^1H\}$ (190 K):** δ 57.2 (br d, $^1J_{RhP}$ = 105). **ESI-**

MS (C_6H_5F): *m/z* 509.2859 [M^+] (calc. 509.2907). **Compound 4**: ^{1}**H:** δ 7.73 (br, 8H, $BAr^F{}_4$), 7.57 (br, 4H, $BAr^F{}_4$), 1.90–1.74 (m, 8H, ^{i}Bu{CH/CH_2}), 1.72–1.63 (m, 4H, ^{i}Bu{CH_2}), 1.14 (dd, 18H, J = 7.5, J = 7.3, ^{t}Bu{Me}), 1.00–(–0.80) (br, 24H, ^{i}Bu{Me}). ^{31}**P**{^{1}**H**}**:** δ 64.5 (br). ^{1}**H (173 K, selected data):** δ 0.25–(–0.38) (at least 4 broad peaks @ 0.05, –0.04, –0.14, –0.25, 6H, ^{i}Bu{Me-agostic}), –22.00 (br d, J = 54.4, 0.63H, RhH), –22.15 (br d, J ~ 50, 0.03H, RhH), –22.83 (br d, J = 55.8, 0.06H, RhH), –23.04 (br d, J = 56.9, 0.28H, RhH). ^{31}**P**{^{1}**H**} **(173 K):** δ 85.7 (dd, $^2J_{PP}$ = 295, $^1J_{RhP}$ = 115, isomer 1), 83.9 (dd, $^2J_{PP}$ = 296, $^1J_{RhP}$ = 114, isomer 2), 78.6 (dd, $^2J_{PP}$ = 299, $^1J_{RhP}$ = 114, isomer 3), 69.8 (dd, $^2J_{PP}$ = 298, $^1J_{RhP}$ = 116, isomer 4), 56.2 2 (dd, $^2J_{PP}$ = 295, $^1J_{RhP}$ = 115, isomer 4), ~49.8 (assumed dd, obscured by isomers at 49.2 and 48.9, outer lines only visible, isomer 3), 49.2 (dd, $^2J_{PP}$ = 296, $^1J_{RhP}$ = 114, isomer 2), 48.9 (dd, $^2J_{PP}$ = 296, $^1J_{RhP}$ = 116, isomer 1). **ESI-MS (C_6H_5F):** *m/z* 507.2760 [M^+] (calc. 507.2750).

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