Cationic (η^5-C_5Me_4R)Rh(III) Complexes with Metalated Aryl Phosphines Featuring η^4-Phosphorus-plus-Pseudoallylic Coordination

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-SUPPPORTING MATERIAL-

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1. Mechanistic proposal for catalytic hydrosilylation

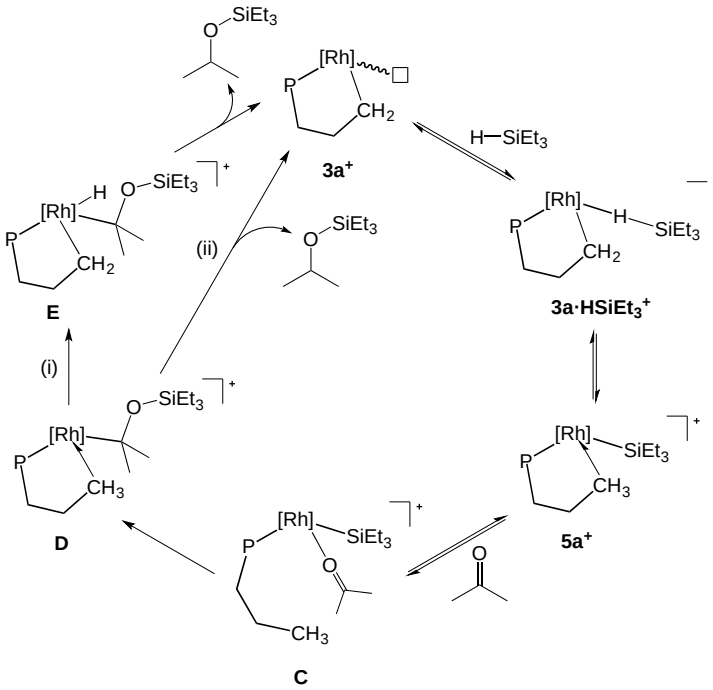


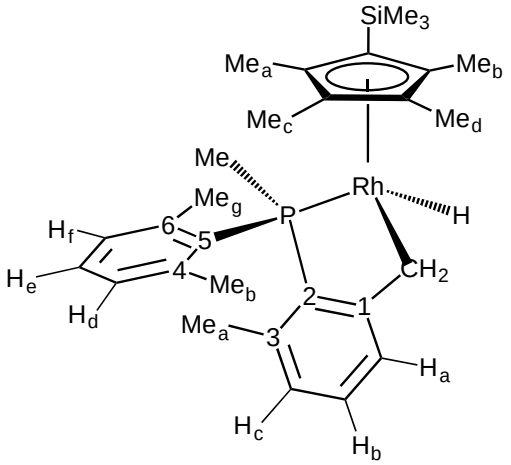
Figure S1. Proposed modified Chalk-Harrod mechanism to account for the hydrosilylation of carbonyl compounds catalyzed by $3a^+$

On the basis of experimental results and taking also into consideration knowledge emanated from the experimental and computational studies discussed earlier for the reactivity of $\mathbf{3a}^+$ toward $SiEt_3H$, Figure S1 depicts a plausible mechanistic path for acetone hydrosilylation with $SiEt_3H$ catalyzed by complex $\mathbf{3a}^+$. The proposed reaction route can be viewed as a variant of the Chalk-Harrod mechanism,[1] and starts with the reaction of $\mathbf{3a}^+$ with $SiEt_3H$ to give an η^1-σ-silane complex, $\mathbf{3a{\cdot}HSiEt_3}^+$. In consonance with our computational studies, the latter could be in equilibrium with an undetected cationic agostic silyl $\mathbf{5a}^+$, i.e. the silyl analogue of the observed hydride $\mathbf{4a}^+$. Disruption of the agostic interaction by acetone (structure **C**) and nucleophilic attack of the silyl group onto the carbonyl carbon atom to produce **D** are expected to be facile transformations and could render the silyl ether product either by sequential oxidative cleavage and reductive coupling steps (route *i*) or by a σ-CAM mechanism (*ii*).[2] The two paths seem reasonable on the basis of the computational studies contained in this contribution.

2. Analytical and spectroscopic data of complexes 2c-2e, 3c-3e, $4c^+$-$4e^+$, $5d^+$, $5e^+$, and $6d^+$.

The purity of the new compounds was established by elemental analysis of the bulk samples for which yields are reported. No additional purification operations were carried out prior to analysis unless otherwise noted.

(η^5-$C_5Me_4SiMe_3$)Rh(H){PMe(2,6-CH_2(Me)C_6H_3)(Xyl)} (1·$SiMe_3$)



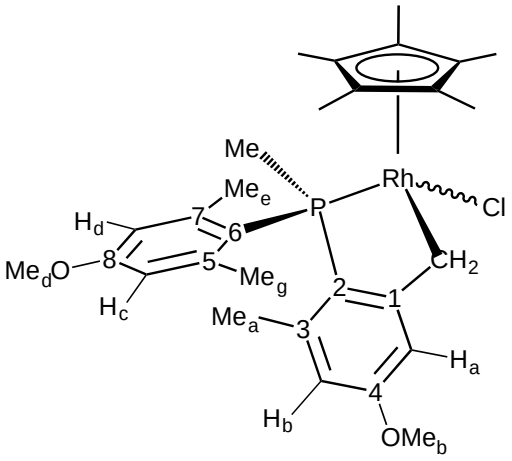
Anal. Calc. for $C_{29}H_{42}PRhSi$: C, 63.0; H, 7.7. **Found:** C, 63.1; H, 7.8.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC) δ: 7.40 (d, 1 H, H_a), 7.04 (td, 1 H, = $^5J_{HP}$ = 2.1 Hz, H_b), 6.94 (td, 1 H, $^5J_{HP}$ = 1.5 Hz, H_e), 6.87, 6.70 (m, 1 H each, H_d, H_f), 6.72 (m, 1 H, H_c), 3.63 (d, 1 H, $^2J_{HH}$ = 14, RhC*H*H), 3.03 (dd, 1 H, $^2J_{HRh}$ = 4.0 Hz, RhCH*H*), 2.34, 1.63 (s, 3 H each, Me_β, Me_γ), 1.93 (d, 3 H, $^2J_{HP}$ = 10.5 Hz, PMe), 1.92, 1.85 (d, 3 H each, $^4J_{HP}$ = 3.0 Hz, Me_a, Me_b), 1.86 (s, 3 H, Me_α), 1.42, 1.22 (s, 3 H each, $^4J_{HP}$ = 2.5 Hz, Me_c, Me_d), 0.50 (s, 9 H, $SiMe_3$), -14.03 (dd, 1 H, $^1J_{RhH}$ = 45.0, $^2J_{HP}$ = 31.0 Hz, RhH). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 ºC) δ: 158.2 (d, $^2J_{CP}$ = 32 Hz, C_1), 142.0, 138.9 (d, $^2J_{CP}$ = 8 Hz, C_4, C_6), 141.6 (dd, $^1J_{CP}$ = 55, $^2J_{CRh}$ = 3 Hz, C_2), 138.8 (C_3), 133.8 (d, $^1J_{CP}$ = 27 Hz, C_5), 130.1, 130.0 (d, $^3J_{CP}$ = 7 Hz, CH_d, CH_f), 129.4 (CH_b), 128.8 (CH_e), 127.4 (d, $^3J_{CP}$ = 17 Hz, CH_a), 127.2 (d, $^3J_{CP}$ = 6 Hz, CH_c), 103.9, 103.8, 103.0, 102.4 (dd, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, $C_q$$Me_a$, $C_q$$Me_b$, $C_q$$Me_c$, $C_q$$Me_d$), 85.5 (dd, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, $C_q$$SiMe_3$), 29.1 (d, $^1J_{CP}$ = 38 Hz, PMe), 25.6, 22.6 (d, $^3J_{CP}$ = 4, $^3J_{CP}$ = 10 Hz, Me_β, Me_γ), 21.6 (dd, $^1J_{CRh}$ = 26, $^2J_{CP}$ = 4 Hz, $RhCH_2$), 20.8 (d, $^3J_{CP}$ = 3 Hz, Me_α), 13.5, 12.7 (Me_a, Me_b), 8.9, 8.8 (Me_c, Me_d), 3.3 ($SiMe_3$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 ºC) δ: 50.8 (d, $^1J_{PRh}$ = 156 Hz).

(η^5-C_5Me_5)Rh(Cl){PMe(2,6-CH_2(Me)-4-OMe-C_6H_2)(2,6-Me_2-4-OMe-C_6H_2)} (2c)



Anal. Calc. for $C_{29}H_{39}ClO_2PRh$**:** C, 59.1; H, 6.7. **Found:** C, 59.3; H, 6.8.

Mayor diastereomer: ^{1}H NMR (400 MHz, 25 ºC, $CDCl_3$) δ: 6.77 (s, 1 H, H_a), 6.65 (s, 1 H, H_d), 6.44 (s, 1 H, H_c), 6.41 (s, 1 H, H_b), 3.77 (s, 3 H, Me_ε), 3.73 (s, 3 H, Me_δ), 3.51 (dt, 1 H, $^2J_{HH}$ = 12.9, $^2J_{HRh}$ = $^3J_{HP}$ = 2.5 Hz, RhC*H*H), 3.36 (dd, 1 H, $^2J_{HRh}$ = 3.5, $^2J_{HH}$ = 12.9 Hz, RhCH*H*), 2.57 (s, 3 H, Me_γ), 2.17 (d, 3 H, $^2J_{HP}$ = 10.3 Hz, PMe), 1.92 (s, 3 H, Me_α), 1.50 (s, 3 H, Me_β), 1.42 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5).

^{13}C{^{1}H} NMR (100 MHz, 25 ºC, $CDCl_3$) δ: 160.7 (C_4), 159.6 (C_7), 158.9 (d, $^2J_{CP}$ = 35 Hz, C_1), 143.73 (d, $^2J_{CP}$ = 11 Hz, C_6), 141.7 (d, $^2J_{CP}$ = 8 Hz, C_8), 139.9 (C_3), 130.2 (dd, $^1J_{CP}$ = 58, $^2J_{CRh}$ = 2 Hz, C_2), 123.2 (d, $^1J_{CP}$ = 38 Hz, C_5), 115.1 (d, $^3J_{CP}$ = 8 Hz, CH_d), 115.0 (d, $^3J_{CP}$ = 8 Hz, CH_c), 114.8 (d, $^3J_{CP}$ = 7 Hz, CH_b), 110.2 (d, $^3J_{CP}$ = 18 Hz, CH_a) 97.9 (t, $^1J_{CRh}$ = $^2J_{CP}$ = 4 Hz, *C*$_5$Me$_5$), 54.9 (Me_δ, Me_ε), 33.8 (dd, $^1J_{CRh}$ = 24, $^2J_{CP}$ = 7 Hz, RhCH_2), 25.9 (d, $^3J_{CP}$ = 5 Hz, Me_γ), 23.5 (d, $^3J_{CP}$ = 7 Hz, Me_β), 20.4 (d, $^3J_{CP}$ = 24 Hz, Me_α), 20.0 (d, $^1J_{CP}$ = 34 Hz, PMe), 8.4 (C_5*Me*$_5$).

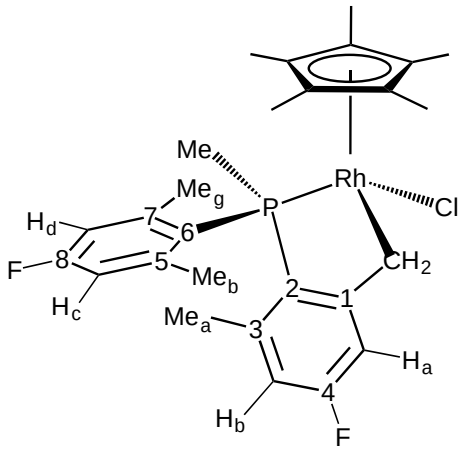
^{31}P{^{1}H} NMR (160 MHz, 25 ºC, $CDCl_3$) δ: 42.2 (d, $^1J_{PRh}$ = 156 Hz).

Minor diastereomer: ^{1}H NMR (400 MHz, 25 ºC, $CDCl_3$) δ: 6.76 (s, 1 H, H_a), 6.66 (s, 1 H, H_d), 6.44 (s, 1 H, H_c), 6.41 (s, 1 H, H_b), 3.77 (s, 3 H, Me_ε), 3.73 (s, 3 H, Me_δ), 3.64 (dt, 1 H, $^2J_{HH}$ = 12.9, $^2J_{HRh}$ = $^3J_{HP}$ = 2.5 Hz, RhC*H*H), 3.35 (dd, 1 H, $^2J_{HRh}$ = 3.5, $^2J_{HH}$ = 12.9 Hz, RhCH*H*), 2.55 (s, 3 H, Me_γ), 2.32 (d, 3 H, $^2J_{HP}$ = 10.3 Hz, PMe), 1.92 (s, 3 H, Me_α), 1.50 (s, 3 H, Me_β), 1.46 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5).

^{13}C{^{1}H} NMR (100 MHz, 25 ºC, $CDCl_3$) δ: 160.7 (C_4), 159.7 (C_7), 159.1 (d, $^2J_{CP}$ = 35 Hz, C_1), 143.6 (d, $^2J_{CP}$ = 10 Hz, C_6), 141.6 (d, $^2J_{CP}$ = 8 Hz, C_8), 139.9 (C_3), 130.3 (dd, $^1J_{CP}$ = 58, $^2J_{CRh}$ = 2 Hz, C_2), 123.6 (d, $^1J_{CP}$ = 38 Hz, C_5), 115.1 (d, $^3J_{CP}$ = 8 Hz, CH_d), 115.0 (d, $^3J_{CP}$ = 8 Hz, CH_c), 114.8 (d, $^3J_{CP}$ = 7 Hz, CH_b), 109.9 (d, $^3J_{CP}$ = 18 Hz, CH_a) 98.0 (t, $^1J_{CRh}$ = $^2J_{CP}$ = 4 Hz, *C*$_5$Me$_5$), 54.9 (Me_δ, Me_ε), 31.8 (dd, $^1J_{CRh}$ = 24, $^2J_{CP}$ = 7 Hz, RhCH_2), 26.1 (d, $^3J_{CP}$ = 5 Hz, Me_γ), 23.5 (d, $^3J_{CP}$ = 7 Hz, Me_β), 22.7 (d, $^1J_{CP}$ = 34 Hz, PMe), 20.4 (d, $^3J_{CP}$ = 2 Hz, Me_α), 8.7 (C_5*Me*$_5$).

^{31}P{^{1}H} NMR (160 MHz, 25 ºC, $CDCl_3$) δ: 40.0 (d, $^1J_{PRh}$ = 156 Hz).

(η^5-C_5Me_5)Rh(Cl){PMe(2,6-CH_2(Me)-4-F-C_6H_2)(2,6-Me_2-4-F-C_6H_2)} (2d)



Anal. Calc. for $C_{27}H_{33}ClF_2PRh$**:** C, 57.4; H, 5.9. **Found:** C, 57.2; H, 6.2.

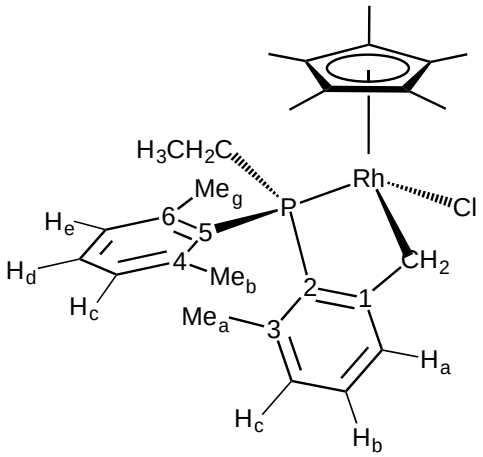
^{1}H NMR (400 MHz, 25 ºC, $CDCl_3$) δ: 6.94 (d, 1 H, $^3J_{HF}$ = 9.5 Hz, H_a), 6.87 (dt, 1 H, $^3J_{HF}$ = 9.5, $^4J_{HP}$ = $^4J_{HH}$ = 2.6 Hz, $H_{c/d}$), 6.65 (dt, 1 H, $^3J_{HF}$ = 9.3, $^4J_{HP}$ = $^4J_{HH}$ = 2.6 Hz, $H_{d/c}$), 6.58 (d, 1 H, $^3J_{HF}$ = 9.6 Hz, H_b), 3.52 (dt, 1 H, $^2J_{HH}$ = 13.5, $^2J_{HRh}$ = $^3J_{HP}$ = 3.0 Hz, RhC*H*H), 3.35 (dd, 1 H, $^2J_{HH}$ = 13.5, $^2J_{HRh}$ = 3.2 Hz, RhCH*H*), 2.60 (s, 3 H, $Me_{\beta/\gamma}$), 2.19 (d, 3 H, $^2J_{HP}$ = 10.1 Hz, PMe), 1.94 (s, 3 H, Me_α), 1.50 (s, 3 H, $Me_{\beta/\gamma}$), 1.42 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5).

^{13}C{^{1}H} NMR (100 MHz, 25 ºC, $CDCl_3$) δ: 163.8 (dd, $^1J_{CF}$ = 251, $^4J_{CP}$ = 2 Hz, C_4), 162.6 (dd, $^1J_{CF}$ = 25, $^4J_{CP}$ = 2 Hz, C_7), 159.9 (dd, $^2J_{CP}$ = 36, $^3J_{CF}$ = 8 Hz, C_1), 144.5, 142.6 (t, $^2J_{CP}$ = $^3J_{CF}$ = 9 Hz, C_6, C_8), 140.8 (d, $^2J_{CF}$ = 9 Hz, C_3), 133.7 (d, $^1J_{CP}$ = 56 Hz, C_2), 127.3 (d, $^1J_{CP}$ = 35 Hz, C_5), 116.7 (dd, $^2J_{CF}$ = 20, $^3J_{CP}$ = 8 Hz, CH_c, CH_d), 114.6 (dd, $^2J_{CF}$ = 22, $^3J_{CP}$ = 8 Hz, CH_b), 113.1 (t, $^2J_{CF}$ = $^3J_{CP}$ = 19 Hz, CH_a), 98.2 (t, $^1J_{CRh}$ = $^2J_{CP}$ = 4 Hz, *C*$_5$Me$_5$), 33.3 (dd, $^1J_{CRh}$ = 24, $^2J_{CP}$ = 7 Hz, Ir*C*H$_2$), 25.8 (d, $^3J_{CP}$ = 5 Hz, $Me_{\beta/\gamma}$), 23.4 (d, $^3J_{CP}$ = 7 Hz, $Me_{\beta/\gamma}$), 20.5 (Me_α), 19.6 (d, $^1J_{CP}$ = 34 Hz, PMe), 8.5 (C_5*Me*$_5$).

^{31}P{^{1}H} NMR (160 MHz, 25 ºC, $CDCl_3$) δ: 43.4 (d, $^1J_{PRh}$ = 157 Hz).

^{19}F{^{1}H} NMR (160 MHz, 25 ºC, $CDCl_3$) δ: -113.0, -114.6 (d, $^5J_{FP}$ = 4 Hz).

(η^5-C_5Me_5)Rh(Cl){PEt(2,6-$CH_2(Me)C_6H_3$)(2,6-$Me_2C_6H_3$)} (2e)



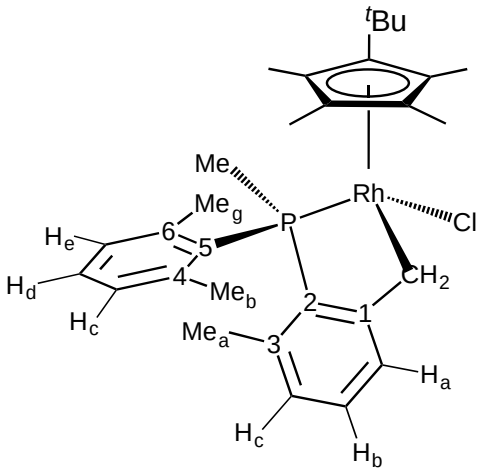
Anal. Calc. for $C_{28}H_{37}ClPRh$**:** C, 61.9; H, 6.9. **Found:** C, 61.7; H, 7.1.

^{1}H NMR (500 MHz, 25 ºC, $CDCl_3$) δ: 7.28 (d, 1 H, $^3J_{HH}$ = 7.5 Hz, H_a), 7.15 (m, 2 H, H_e, $H_{d/f}$), 7.10 (dt, 1 H, $^3J_{HH}$ = 7.2 Hz, $^5J_{HP}$ = 2 Hz, H_b), 6.87 (d, 1 H, $^3J_{HH}$ = 7.2, $H_{f/d}$), 6.80 (dd, 1 H, $^3J_{HH}$ = 7.4, $^4J_{HP}$ = 2.9 Hz, H_c), 3.71 (dd, 1 H, $^2J_{HH}$ = 13.5, $^3J_{HP}$ = 3.1 Hz, RhC*H*H), 3.43 (dd, 1 H, $^2J_{HH}$ = 13.4, $^2J_{HRh}$ = 3.4 Hz, RhCH*H*), 3.03 (dq, 1 H, $^3J_{HH}$ = 6.8, $^2J_{HP}$ = 21.9 Hz, PCH*H*CH_3), 2.62 (s, 3 H, $Me_{\beta/\gamma}$), 2.36 (dq, 1 H, $^3J_{HH}$ = 6.9, $^2J_{HP}$ = 21.3 Hz, PC*H*HCH_3), 1.96 (s, 3 H, Me_α), 1.49 (s, 3 H, $Me_{\beta/\gamma}$), 1.34 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5), 0.72 (dt, 3 H, $^3J_{HH}$ = 7.3, $^3J_{HH}$ = 18.1 Hz, PCH_2CH_3).

^{13}C{^{1}H} NMR (125 MHz, 25 ºC, $CDCl_3$) δ: 158.6 (d, $^2J_{CP}$ = 34 Hz, C_1), 141.6 (d, $^2J_{CP}$ = 7 Hz, $C_{4/6}$), 140.7 (d, $^2J_{CP}$ = 9 Hz, $C_{6/4}$), 140.5 (C_3), 134.9 (dd, $^1J_{CP}$ = 52, $^2J_{CRh}$ = 3 Hz, C_2), 133.1 (d, $^1J_{CP}$ = 31 Hz, C_5), 130.3 (d, $^3J_{CP}$ = 8 Hz, $CH_{d/f}$), 129.7 (d, $^4J_{CP}$ = 2 Hz, CH_b), 129.6 (d, $^3J_{CP}$ = 7 Hz, $CH_{f/d}$), 129.2 (CH_e), 126.9 (d, $^3J_{CP}$ = 17 Hz, CH_a), 126.6 (d, $^3J_{CP}$ = 6 Hz, CH_c), 98.9 (t, $^2J_{CP}$ = $^1J_{CRh}$ = 4 Hz, *C*$_5$Me$_5$), 33.8 (dd, $^1J_{CRh}$ = 25, $^2J_{CP}$ = 8 Hz, Rh*C*H_2), 26.1 (d, $^3J_{CP}$ = 5 Hz, $Me_{\beta/\gamma}$), 24.6 (d, $^1J_{CP}$ = 39 Hz, P*C*H_2CH_3), 24.5 (d, $^3J_{CP}$ = 4 Hz, $Me_{\gamma/\beta}$), 20.8 (d, $^3J_{CP}$ = 2 Hz, Me_α), 12.0 (d, $^2J_{CP}$ = 2 Hz, PCH_2CH_3), 8.8 (C_5Me_5).

^{31}P{^{1}H} NMR (200 MHz, 25 ºC, $CDCl_3$) δ: 59.6 (d, $^1J_{PRh}$ = 156 Hz).

(η^5-$C_5Me_4{}^tBu$)Rh(H){PMe(2,6-CH_2(Me)C_6H_3)(Xyl)} (2f)



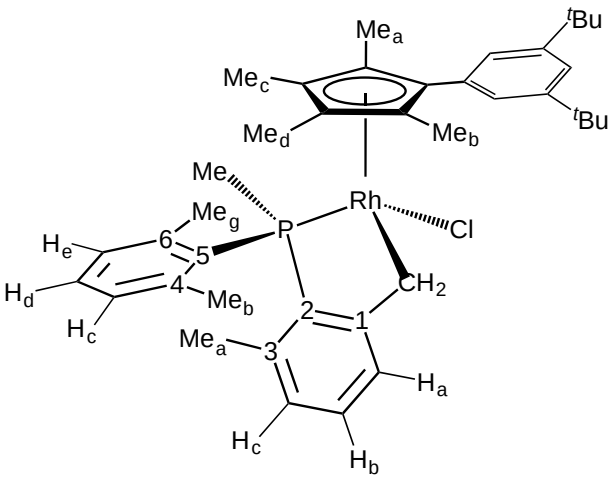
Anal. Calc. for $C_{30}H_{41}ClPRh$: C, 63.1; H, 7.2. **Found:** C, 63.4; H, 7.2.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC) δ: 7.41 (d, 1 H, H_a), 7.04 (td, 1 H, $^5J_{HP}$ = 2.1 Hz, H_b), 6.92 (td, 1 H, $^5J_{HP}$ = 1.5 Hz, H_e), 6.84, 6.62 (m, 1 H each, H_d, H_f), 6.72 (m, 1 H, H_c), 4.22 (dt, 1 H, $^2J_{HH}$ = 12.5, $^2J_{HRh}$ = $^3J_{HP}$ = 3.0 Hz, RhC*H*H), 3.64 (dd, 1 H, $^2J_{HRh}$ = 3.5 Hz, RhCH*H*), 2.38, 1.45 (s, 3 H each, Me_β, Me_γ), 2.30 (d, 3 H, $^2J_{HP}$ = 10.5 Hz, PMe), 1.84, 1.53 (d, 3 H each, $^4J_{HP}$ = 3.0 Hz, Me_a, Me_b), 1.83 (s, 3 H, Me_α), 1.56 (s, 9 H, ^{t}Bu), 1.03, 0.86 (d, 3 H each, $^4J_{HP}$ = 2.5 Hz, Me_c, Me_d). All aromatic couplings are of *ca.* $^3J_{HH}$ ≈ 7.5 Hz.

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 ºC) δ: 157.9 (d, $^2J_{CP}$ = 32 Hz, C_1), 142.4, 140.1 (d, $^2J_{CP}$ = 8 Hz, C_4, C_6), 139.6 (C_3), 139.3 (dd, $^1J_{CP}$ = 53, $^2J_{CRh}$ = 3 Hz, C_2), 132.7 (d, $^1J_{CP}$ = 30 Hz, C_5), 130.5, 130.1 (d, $^3J_{CP}$ = 7 Hz, CH_d, CH_f), 129.9 (CH_b), 129.5 (CH_e), 127.8 (d, $^3J_{CP}$ = 7 Hz, CH_c), 127.5 (d, $^3J_{CP}$ = 17 Hz, CH_a), 111.2 (dd, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, C_q ^{t}Bu), 105.4, 101.3, 97.3, 89.1 (dd, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, $C_q$$Me_a$, $C_q$$Me_b$, $C_q$$Me_c$, $C_q$$Me_d$), 34.3 (dd, $^1J_{CRh}$ = 24, $^2J_{CP}$ = 6 Hz, $RhCH_2$), 34.5 (CMe_3), 32.4 (^{t}Bu), 26.0, 23.7 (d, $^3J_{CP}$ = 5, $^3J_{CP}$ = 8 Hz, resp., Me_β, Me_γ), 20.6 (d, $^3J_{CP}$ = 2 Hz, Me_α), 20.5 (d, $^1J_{CP}$ = 34 Hz, PMe), 13.1, 12.5 (Me_a, Me_b), 8.7, 8.2 (Me_c, Me_d).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 ºC) δ: 46.9 (d, $^1J_{PRh}$ = 156 Hz).

(η^5-$C_5Me_4Ar^{Bu^t_2}$)Rh(H){PMe(2,6-CH_2(Me)C_6H_3)(Xyl)} (2g)



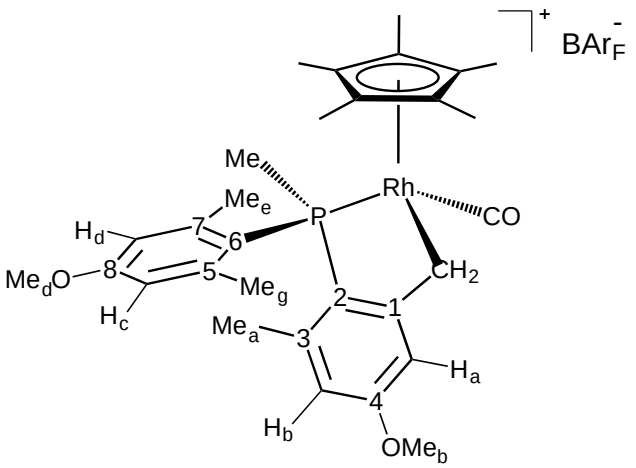
Anal. Calc. for $C_{40}H_{53}ClPRh$: C, 68.3; H, 7.6. **Found:** C, 68.4; H, 7.5.

^{1}H NMR (400 MHz, C_6D_6, 25 ºC) δ: 7.67 (d, 2 H, $^4J_{HH}$ = 2.0 Hz, *o*-CH_{Ar}), 7.46 (t, 1 H, $^4J_{HH}$ = 2.0 Hz, *p*-CH_{Ar}), 7.43 (d, 1 H, H_a), 7.03 (td, 1 H, $^5J_{HP}$ = 1.9 Hz, H_b), 6.85 (td, 1 H, $^5J_{HP}$ = 1.3 Hz, H_e), 6.71, 6.58 (m, 1 H each, H_d, H_f), 6.69 (m, 1 H, H_c), 4.13 (dt, 1 H, $^2J_{HH}$ = 13.0, $^2J_{HRh}$ = $^3J_{HP}$ = 2.5 Hz, RhC*H*H), 3.72 (dd, 1 H, $^2J_{HRh}$ = 3.5 Hz, RhCH*H*), 2.21 (d, 3 H, $^2J_{HP}$ = 10.5 Hz, PMe), 1.96, 1.56, 1.11, 0.77 (d, 3 H each, $^4J_{HP}$ = 3.0 Hz, Me_a, Me_b, Me_c, Me_d), 1.82 (s, 3 H, Me_α), 1.78, 1.44 (s, 3 H each, Me_β, Me_γ), 1.41 (s, 18 H, ^{t}Bu). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 ºC) δ: 158.0 (d, $^2J_{CP}$ = 32 Hz, C_1), 150.6 (*m*-C_qAr), 142.2, 141.2 (d, $^2J_{CP}$ = 8 Hz, C_4, C_6), 139.4 (C_3), 139.0 (dd, $^1J_{CP}$ = 54, $^2J_{CRh}$ = 2 Hz, C_2), 133.8 (C_qAr), 132.5 (d, $^1J_{CP}$ = 33 Hz, C_5), 130.1, 129.5 (d, $^3J_{CP}$ = 7 Hz, CH_d, CH_f), 129.9 (CH_b), 129.4 (CH_e), 127.7 (d, $^3J_{CP}$ = 7 Hz, CH_c), 127.6 (d, $^3J_{CP}$ = 16 Hz, CH_a), 125.7 (*o*-CH_{Ar}), 120.5 (*p*-CH_{Ar}), 112.8, 101.1, 100.0, 95.2, 89.6 (dd, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, $C_q$$C_5$$Me_4$, $C_q$$Me_a$, $C_q$$Me_b$, $C_q$$Me_c$, $C_q$$Me_d$), 35.8 (dd, $^1J_{CRh}$ = 24, $^2J_{CP}$ = 6 Hz, $RhCH_2$), 35.3 (CMe_3), 31.9 (^{t}Bu), 24.2, 23.4 (d, $^3J_{CP}$ = 6 Hz, Me_β, Me_γ), 20.8 (Me_α), 18.8 (d, $^1J_{CP}$ = 34 Hz, PMe), 10.8, 8.6, 8.7, 8.1 (Me_a, Me_b, Me_c, Me_d).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 ºC) δ: 46.7 (d, $^1J_{PRh}$ = 154 Hz).

(η^5-C_5Me_5)Rh(CO){PMe(2,6-CH_2(Me)-4-OMe-C_6H_2)(2,6-Me_2-4-OMe-C_6H_2)} (3c·CO^+)



IR (Nujol): 2050 cm^{-1}.

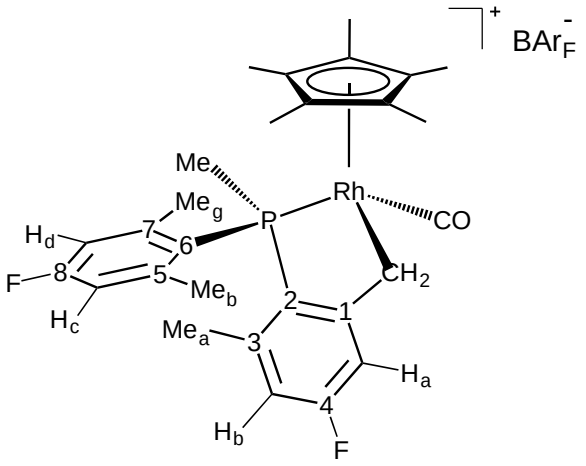
Anal. Calc. for $C_{62}H_{51}BF_{24}O_3PRh$**:** C, 51.5; H, 3.6. **Found:** C, 51.4; H, 3.6.

^{1}H NMR (500 MHz, 25 ºC, CD_2Cl_2) δ: 6.87 (s, 1 H, H_a), 6.82 (t, 1 H, $^4J_{HP}$ = $^4J_{HH}$ = 2.9 Hz, $H_{c/d}$), 6.67 (t, 1 H, $^4J_{HP}$ = $^4J_{HH}$ = 2.8 Hz, $H_{d/c}$), 6.64 (t, 1 H, $^4J_{HP}$ = $^4J_{HH}$ = 3.0 Hz, H_b), 3.85, 3.84 (s, 3 H, 2 OMe), 3.49 (dd, 1 H, $^2J_{HH}$ = 12.6, $^2J_{HRh}$ = 2.1 Hz, RhC*H*H), 3.29 (dd, 1 H, $^2J_{HH}$ = 12.6, $^2J_{HRh}$ = 4.2 Hz, RhCH*H*), 2.52 (s, 3 H, $Me_{\beta/\gamma}$), 2.35 (dd, 3 H, $^2J_{HP}$ = 9.7, $^3J_{HRh}$ = 1.3 Hz, PMe), 2.04 (s, 3 H, Me_α), 1.72 (d, 15 H, $^4J_{HP}$ = 2.8 Hz, C_5Me_5), 1.56 (s, 3 H, $Me_{\gamma/\beta}$).

^{13}C{^{1}H} NMR (125 MHz, 25 ºC, CD_2Cl_2) δ: 189.1 (dd, $^1J_{CRh}$ = 74, $^2J_{CP}$ = 19 Hz, CO), 162.9, 162.2 (d, $^4J_{CP}$ = 3 Hz, C_4, C_7), 154.7 (d, $^2J_{CP}$ = 31 Hz, C_1), 144.8 (d, $^2J_{CP}$ = 11 Hz, $C_{6/8}$), 143.0 (d, $^2J_{CP}$ = 10 Hz, $C_{8/6}$), 141.7 (dd, $^2J_{CP}$ = 3, $^3J_{CRh}$ = 2 Hz, C_3), 127.6 (dd, $^1J_{CP}$ = 65, $^2J_{CRh}$ = 3 Hz, C_2), 116.8 (d, $^3J_{CP}$ = 9 Hz, CH_b), 116.7 (d, $^1J_{CP}$ = 48 Hz, C_5), 116.6 (d, $^3J_{CP}$ = 10 Hz, CH_c, CH_d), 110.8 (dd, $^3J_{CP}$ = 18, $^3J_{CRh}$ = 2 Hz, CH_a), 106.4 (dd, $^1J_{CRh}$ = 4, $^2J_{CP}$ = 2 Hz, *C*$_5$Me$_5$), 55.7, 55.6 (Me_δ, Me_ε), 28.5 (d, $^1J_{CRh}$ = 22 Hz, RhCH_2), 26.2 (d, $^3J_{CP}$ = 5 Hz, $Me_{\beta/\gamma}$), 26.1 (d, $^1J_{CP}$ = 40 Hz, PMe), 23.8 (d, $^3J_{CP}$ = 8 Hz, $Me_{\gamma/\beta}$), 20.7 (d, $^3J_{CP}$ = 3 Hz, Me_α), 9.0 (C$_5$*Me*$_5$).

^{31}P{^{1}H} NMR (200 MHz, 25 ºC, CD_2Cl_2) δ: 33.8 (d, $^1J_{PRh}$ = 125 Hz).

(η^5-C_5Me_5)Rh(CO){PMe(2,6-CH_2(Me)-4-F-C_6H_2)(2,6-Me_2-4-F-C_6H_2)} (3d·CO^+)



IR (Nujol): 2060 cm^{-1}.

Anal. Calc. for $C_{60}H_{45}BF_{26}OPRh$**:** C, 50.7; H, 3.2. **Found:** C, 50.5; H, 3.2.

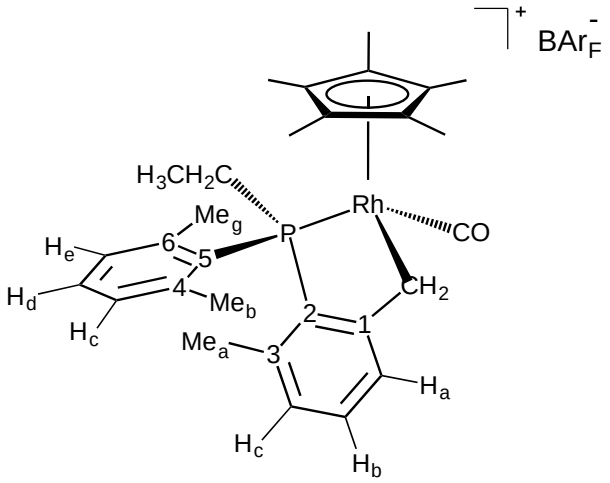
^{1}H NMR (400 MHz, 25 ºC, CD_2Cl_2) δ: 7.11 (d, 1 H, $^3J_{HF}$ = 10.5 Hz, H_a), 7.08 (d, 1 H, $^3J_{HF}$ = 10.5 Hz, $H_{c/d}$), 6.90 (m, 2 H, H_b, $H_{d/c}$), 3.54 (d, 1 H, $^2J_{HH}$ = 12.9 Hz, RhC*H*H), 3.29 (dd, 1 H, $^2J_{HH}$ = 12.9, $^3J_{HRh}$ = 3.9 Hz, RhCH*H*), 2.57 (s, 3 H, $Me_{\beta/\gamma}$), 2.39 (d, 3 H, $^2J_{HP}$ = 9.5 Hz, PMe), 2.08 (s, 3 H, Me_α), 1.73 (d, 15 H, $^4J_{HP}$ = 2.9 Hz, C_5Me_5), 1.60 (s, 3 H, $Me_{\gamma/\beta}$).

^{13}C{^{1}H} NMR (100 MHz, 25 ºC, CD_2Cl_2) δ: 188.1 (d, $^1J_{CRh}$ = 73, $^2J_{CP}$ = 19 Hz, CO), 165.0 (dd, $^1J_{CF}$ = 254, $^4J_{CP}$ = 3 Hz, C_4), 164.1 (dd, $^1J_{CF}$ = 255, $^4J_{CP}$ = 3 Hz, C_7), 155.3 (dd, $^2J_{CP}$ = 32, $^3J_{CF}$ = 9 Hz, C_1), 145.3 (t, $^2J_{CP}$ = $^3J_{CF}$ = 10 Hz, $C_{6/8}$), 143.8 (t, $^2J_{CP}$ = $^3J_{CF}$ = 9 Hz, $C_{8/6}$), 142.6 (dd, $^3J_{CF}$ = 9, $^2J_{CP}$ = 3 Hz, C_3), 131.3 (d, $^1J_{CP}$ = 62 Hz, C_2), 120.9 (d, $^1J_{CP}$ = 42 Hz, C_5), 118.1, 117.9 (dd, $^2J_{CF}$ = 20, $^3J_{CP}$ = 10 Hz, CH_c, CH_d), 117.2 (dd, $^2J_{CF}$ = 22, $^3J_{CP}$ = 9 Hz, CH_b), 113.2 (t, $^2J_{CF}$ = $^3J_{CP}$ = 20 Hz, CH_a), 106.4 (*C*$_5$Me$_5$), 27.3 (d, $^1J_{CRh}$ = 21 Hz, Ir*C*H_2), 25.6 (d, $^3J_{CP}$ = 5 Hz, $Me_{\beta/\gamma}$), 25.2 (d, $^1J_{CP}$ = 40 Hz, PMe), 23.5 (d, $^3J_{CP}$ = 8 Hz, $Me_{\gamma/\beta}$), 20.3 (Me_α), 8.6 (C_5*Me*$_5$).

^{31}P{^{1}H} NMR (160 MHz, 25 ºC, CD_2Cl_2) δ: 34.7 (dd, $^1J_{PRh}$ = 128, $^5J_{PF}$ = 3 Hz).

^{19}F{^{1}H} NMR (160 MHz, 25 ºC, CD_2Cl_2) δ: -108.2, -110.4 (d, $^5J_{FP}$ = 3 Hz).

(η^5-C_5Me_5)Rh(CO){PEt(2,6-CH_2(Me)C_6H_3)(2,6-$Me_2C_6H_3$)} (3e·CO^+)



IR (Nujol): 2054 cm^{-1}.

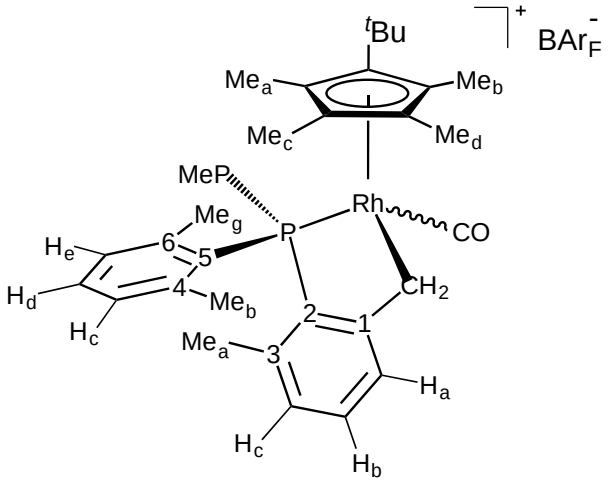
Anal. Calc. for $C_{61}H_{49}BF_{24}OPRh$**:** C, 52.4; H, 3.5. **Found:** C, 52.5; H, 3.6.

^{1}H NMR (500 MHz, 25 ºC, CD_2Cl_2) δ: 7.39 (m, 3 H, 3 H_{ar}), 7.30 (m, 1 H, H_{ar}), 7.08 (m, 2 H, 2 H_{ar}), 3.65 (dd, 1 H, $^2J_{HH}$ = 12.9, $^3J_{HP}$ = 2.1 Hz, RhC*H*H), 3.25 (dd, 1 H, $^2J_{HH}$ = 12.9, $^2J_{HRh}$ = 4.0 Hz, RhCH*H*), 2.94 (m, 1 H, PCH*H*CH_3), 2.75 (m, 1 H, PC*H*HCH_3), 2.55 (s, 3 H, $Me_{\beta/\gamma}$), 2.00 (s, 3 H, Me_α), 1.66 (d, 15 H, $^4J_{HP}$ = 2.8 Hz, C_5Me_5), 1.52 (s, 3 H, $Me_{\beta/\gamma}$), 0.65 (dt, 3 H, $^3J_{HH}$ = 7.5, $^3J_{HP}$ = 19.9 Hz, PCH_2CH_3).

^{13}C{^{1}H} NMR (125 MHz, 25 ºC, CD_2Cl_2) δ: 19.2 (dd, $^1J_{CRh}$ = 73, $^2J_{CP}$ = 19 Hz, CO), 153.9 (d, $^2J_{CP}$ = 28 Hz, C_1), 142.3 (d, $^2J_{CP}$ = 8 Hz, $C_{4/6}$), 141.4 (t, $^2J_{CP}$ = $^4J_{CRh}$ = 1 Hz, C_3), 140.7 (d, $^2J_{CP}$ = 9 Hz, $C_{6/4}$), 132.3, 132.0 (d, $^4J_{CP}$ = 3 Hz, CH_b, CH_e), 131.4, 131.0 (d, $^3J_{CP}$ = 9 Hz, CH_d, CH_f), 131.0 (dd, $^1J_{CP}$ = 57, $^2J_{CRh}$ = 3 Hz, C_5), 129.3 (d, $^3J_{CP}$ = 7 Hz, CH_c), 126.9 (dd, $^3J_{CP}$ = 17, $^4J_{CRh}$ = 2 Hz, CH_a), 126.7 (d, $^1J_{CP}$ = 38 Hz, C_2), 106.9 (bs, *C*$_5$Me$_5$), 28.6 (d, $^1J_{CP}$ = 34 Hz, P*C*H$_2$CH$_3$), 27.9 (dd, $^1J_{CRh}$ = 21, $^2J_{CP}$ = 2 Hz, Rh*CH$_2$*), 26.3 (d, $^3J_{CP}$ = 5 Hz, $Me_{\beta/\gamma}$), 24.4 (d, $^3J_{CP}$ = 7 Hz, $Me_{\gamma/\beta}$), 20.4 (d, $^3J_{CP}$ = 3 Hz, Me_α), 9.2 (d, $^2J_{CP}$ = 3 Hz, PCH$_2$*C*H$_3$), 8.9 (C$_5$*Me*$_5$).

^{31}P{^{1}H} NMR (200 MHz, 25 ºC, CD_2Cl_2) δ: 54.2 (d, $^1J_{PRh}$ = 126 Hz).

(η^5-$C_5Me_4{}^tBu$)Rh(H){PMe(2,6-CH_2(Me)C_6H_3)(Xyl)} (3f·CO^+)



Anal. Calc. for $C_{63}H_{53}BF_{24}OPRh$: C, 53.0; H, 3.7. **Found:** C, 52.9; H, 3.7.

Mayor isomer (*syn*): IR (Nujol): ν(C-O) 2050 cm^{-1}.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.39 (td, 1 H, $^5J_{HP}$ = 2.1 Hz, H_e), 7.36 (d, 1 H, H_a), 7.34 (td, 1 H, $^5J_{HP}$ = 2.5 Hz, H_b), 7.28, 7.07 (m, 1 H each, H_d, H_f), 7.10 (m, 1 H, H_c), 3.60 (dt, 1 H, $^2J_{HH}$ = 12.0, $^2J_{HRh}$ = $^3J_{HP}$ = 2.0 Hz, RhC*H*H), 3.38 (dd, 1 H, $^2J_{HRh}$ = 4.0 Hz, RhCH*H*), 2.56, 1.53 (s, 3 H each, Me_β, Me_γ), 2.42 (dd, 3 H, $^2J_{HP}$ =10.5, $^3J_{HRh}$ = 1.0 Hz, PMe), 2.05, 1.88 (d, 3 H each, $^4J_{HP}$ = 3.0 Hz, Me_a, Me_b), 2.05 (s, 3 H, Me_α), 1.50 (s, 9 H, ^{t}Bu), 1.40, 1.20 (d, 3 H each, $^4J_{HP}$ = 2.5 Hz, Me_c, Me_d). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 189.3 (dd, $^1J_{CRh}$ = 73, $^2J_{CP}$ = 18 Hz, CO), 152.2 (d, $^2J_{CP}$ = 32 Hz, C_1), 142.6, 140.8 (d, $^2J_{CP}$ = 9 Hz, C_4, C_6), 140.6 (C_3), 135.6 (dd, $^1J_{CP}$ = 58, $^2J_{CRh}$ = 3 Hz, C_2), 132.5 (d, $^4J_{CP}$ = 2 Hz, CH_e), 132.1 (d, $^4J_{CP}$ = 2 Hz, CH_b), 131.7, 131.3 (d, $^3J_{CP}$ = 9 Hz, CH_d, CH_f), 130.3 (d, $^3J_{CP}$ = 8 Hz, CH_c), 126.6 (d, $^3J_{CP}$ = 16 Hz, CH_a), 125.4 (d, $^1J_{CP}$ = 50 Hz, C_5), 120.2 (d, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, C_q ^{t}Bu), 108.8, 106.6, 106.0, 105.9 (da, $^1J_{CRh}$ = 3 Hz, $C_q$$Me_a$, $C_q$$Me_b$, $C_q$$Me_c$, $C_q$$Me_d$), 34.3 (*C*$Me_3$), 32.6 (^{t}Bu), 29.5 (da, $^1J_{CH}$ = 134, $^1J_{CRh}$ = 24, RhCH_2), 26.2, 23.8 (d, $^3J_{CP}$ = 5, $^3J_{CP}$ = 8 Hz, resp., Me_β, Me_γ), 25.3 (d, $^1J_{CP}$ = 39 Hz, PMe), 20.5 (d, $^3J_{CP}$ = 3 Hz, Me_α), 13.0, 12.9 (Me_a, Me_b), 8.3, 8.0 (Me_c, Me_d).

^{13}C NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 29.5 (pseudo dt, $^1J_{CH}$ = 134 Hz, RhCH_2).

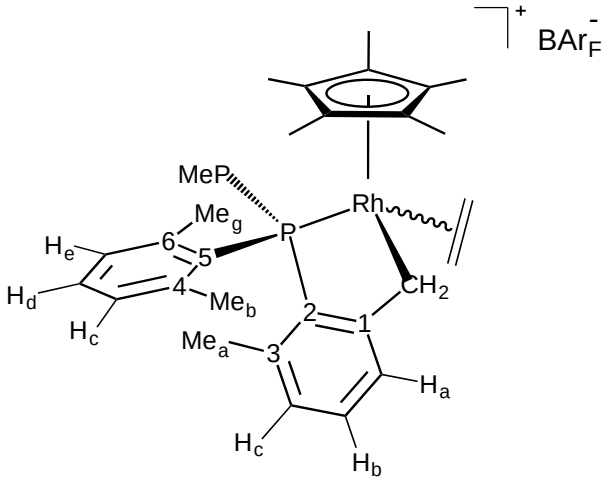
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 37.6 (d, $^1J_{PRh}$ = 126 Hz).

Minor isomer (*anti*): IR (Nujol): ν(C-O) 2045 cm^{-1}.

^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) δ: 4.05 (dt, 1 H, $^2J_{HH}$ = 13.0, $^2J_{HRh}$ = $^3J_{HP}$ =2.5 Hz, RhC*H*H), 2.82 (dd, 1 H, $^2J_{HRh}$ = 3.3 Hz, RhCH*H*), 2.64, 1.72 (s, 3 H each, Me_β, Me_γ), 2.25 (d, 3 H, $^2J_{HP}$ = 9.5 Hz, PMe), 2.19, 2.01 (d, 3 H each, $^4J_{HP}$ = 3.0 Hz, Me_a, Me_b), 1.82 (s, 3 H, Me_α), 1.75, 1.36 (d, 3 H each, $^4J_{HP}$ = 2.5 Hz, Me_c, Me_d), 1.41 (s, 9 H, ^{t}Bu).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 32.6 (d, $^1J_{PRh}$ = 128 Hz).

(η^5-C_5Me_5)Rh(C_2H_4){PMe(2,6-CH_2(Me)C_6H_3)(2,6-$Me_2C_6H_3$)} (3a·$C_2H_4^+$)



Anal. Calc. for $C_{61}H_{51}BF_{24}PRh$: C, 52.9; H, 3.7; **Found:** C, 52.8; H, 3.4.

Syn isomer: **^{1}H NMR** (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.40 (d, 1 H, H_a), 7.34 (td, 1 H, $^5J_{HP}$ = 1.7 Hz, H_e), 7.29 (td, 1 H, $^5J_{HP}$ = 2.5 Hz, H_b), 7.23, 7.08 (m, 1 H each, H_d, H_f), 7.04 (m, 1 H, H_c), 3.80 (dd, 1 H, $^2J_{HH}$ = 12.0, $^2J_{HRh}$ = 3.5 Hz, RhC*H*H), 3.62 (dd, 1 H, $^2J_{HRh}$ = 3.5 Hz, RhCH*H*), 3.22, 2.90 (m, 2 H each, C_2H_4), 2.45, 1.62 (s, 3 H each, Me_β, Me_γ), 2.04 (s, 3 H, Me_α), 1.79 (d, 3 H, $^2J_{HP}$ = 9.7 Hz, PMe), 1.44 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 153.5 (d, $^2J_{CP}$ = 30 Hz, C_1), 141.5, 140.6 (d, $^2J_{CP}$ = 9 Hz, C_4, C_6), 140.5 (C_3), 135.1 (dd, $^1J_{CP}$ = 54, $^2J_{CRh}$ = 2 Hz, C_2), 131.7 (d, $^4J_{CP}$ = 2 Hz, CH_b), 131.4 (d, $^4J_{CP}$ = 2 Hz, CH_e), 131.0 (d, $^3J_{CP}$ = 8 Hz, CH_d, CH_f), 130.3 (d, $^3J_{CP}$ = 6 Hz, CH_c), 127.7 (d, $^1J_{CP}$ = 38 Hz, C_5), 126.5 (d, $^3J_{CP}$ = 16 Hz, CH_a), 105.0 (C_5Me_5), 65.0 (d, $^1J_{CRh}$ = 8.5 Hz, C_2H_4), 33.7 (dd, $^1J_{CRh}$ = 21, $^2J_{CP}$ = 4 Hz, $RhCH_2$), 25.9, 24.3 (d, $^3J_{CP}$ = 7 Hz, Me_β, Me_γ), 20.7 (d, $^3J_{CP}$ = 3 Hz, Me_α), 16.7 (d, $^1J_{CP}$ = 36 Hz, PMe), 8.0 (C_5Me_5).

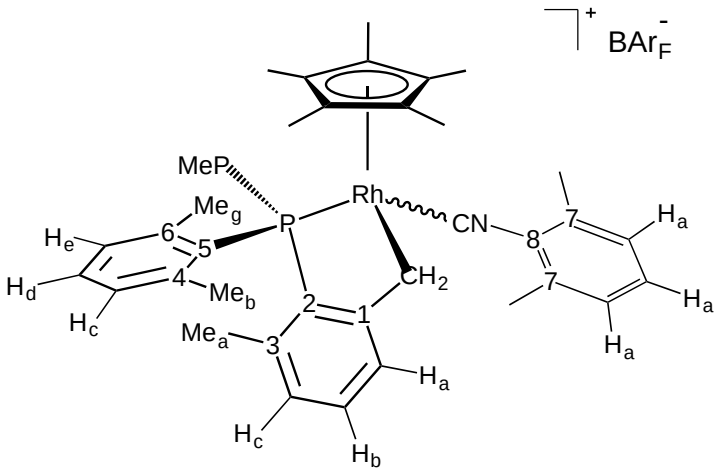
^{13}C NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 65.0 (t, $^1J_{CH}$ = 162 Hz, C_2H_4), 33.7 (pseudo td, $^1J_{CH}$ = 137 Hz, $RhCH_2$).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 39.6 (d, $^1J_{PRh}$ = 140 Hz).

Anti isomer: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 3.45 (dd, 1 H, $^2J_{HH}$ = 12.0, $^2J_{HRh}$ = 3.5 Hz, RhC*H*H), 3.31 (dd, 1 H, $^2J_{HRh}$ = 3.4 Hz, RhCH*H*), 2.90, 2.76 (m, 2 H each, C_2H_4), 2.58, 1.55 (s, 3 H each, Me_β, Me_γ), 2.23 (d, 3 H, $^2J_{HP}$ = 9.7 Hz, PMe), 2.13 (s, 3 H, Me_α), 1.68 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 38.3 (d, $^1J_{PRh}$ = 137 Hz).

(η^5-C_5Me_5)Rh(CNXyl){PMe(2,6-CH_2(Me)C_6H_3)(2,6-$Me_2C_6H_3$)} (3a·CNXyl$^+$)



Anal. Calc. for $C_{68}H_{56}BF_{24}NPRh$: C, 54.9; H, 3.8; N, 0.9. **Found:** C, 54.8; H, 3.6; N, 1.2.

Syn isomer: IR (Nujol): ν(C-N) 2150 cm^{-1}.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.35 (m, 2 H, H_a, H_e), 7.26, 7.06 (m, 3 H, H_b, H_d, H_f), 7.18 (t, 1 H, H_h), 7.07 (d, 2 H, H_g), 7.00 (m, 1 H, H_c), 3.49 (d, 1 H, $^2J_{HH}$ = 12.5 Hz, RhC*H*H), 3.36 (dd, 1 H, $^2J_{HRh}$ = 3.6 Hz, RhCH*H*), 2.58, 1.55 (s, 3 H each, Me_β, Me_γ), 2.24 (d, 3 H, $^2J_{HP}$ = 8.3 Hz, PMe), 2.17 (s, 6 H, Me_{cyn}), 2.02 (s, 3 H, Me_α), 1.68 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

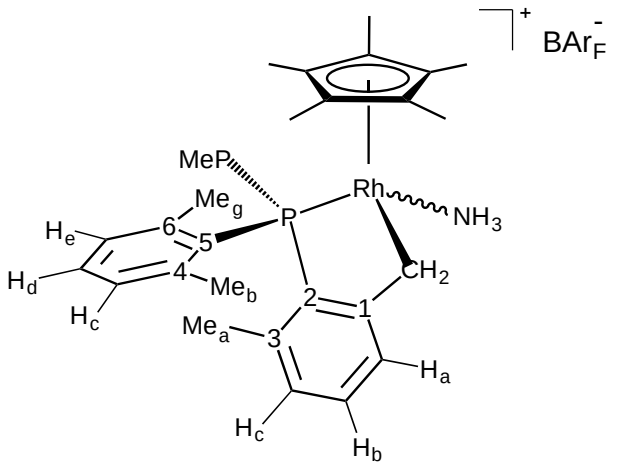
^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 154.0 (d, $^2J_{CP}$ = 33 Hz, C_1), 152.5 (m, C≡N), 142.3, 140.4 (d, $^2J_{CP}$ = 10 Hz, C_4, C_6), 140.5 (C_3), 137.0 (dd, $^1J_{CP}$ = 57, $^2J_{CRh}$ = 3 Hz, C_2), 135.4 (C_7), 131.5 (d, $^4J_{CP}$ = 3 Hz, CH_b), 131.4 (d, $^4J_{CP}$ = 3 Hz, CH_e), 131.1, 130.9 (d, $^3J_{CP}$ = 8 Hz, CH_d, CH_f), 130.0 (CH_h), 129.6 (d, $^3J_{CP}$ = 6 Hz, CH_c), 128.6 (CH_g), 127.4 (d, $^1J_{CP}$ = 38 Hz, C_5), 126.7 (d, $^3J_{CP}$ = 16 Hz, CH_a), 103.5 (sa, C_5Me_5), 28.6 (dd, $^1J_{CRh}$ = 22, $^2J_{CP}$ = 2 Hz, $RhCH_2$), 26.0, 23.4 (d, $^3J_{CP}$ = 8, $^3J_{CP}$ = 6 Hz, resp., Me_β, Me_γ), 24.7 (d, $^1J_{CP}$ = 30 Hz, PMe), 20.5 (d, $^3J_{CP}$ = 3 Hz, Me_α), 18.6 (Me_{cyn}), 8.99 (C_5Me_5).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 40.0 (d, $^1J_{PRh}$ = 133 Hz).

Anti isomer: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 3.86 (d, 1 H, $^2J_{HH}$ = 12.5 Hz, RhC*H*H), 2.95 (dd, 1 H, $^2J_{HRh}$ = 3.5 Hz, RhCH*H*), 2.67, 1.67 (s, 3 H each, Me_β, Me_γ), 2.26 (s, 3 H, Me_α), 2.20 (d, 3 H, $^2J_{HP}$ = 9.5 Hz, PMe), 1.84 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 33.9 (d, $^1J_{PRh}$ = 132 Hz).

(η^5-C_5Me_5)Rh(NH_3){PMe(2,6-CH_2(Me)C_6H_3)(2,6-$Me_2C_6H_3$)} (3a·NH_3^+)



Anal. Calc. for $C_{59}H_{50}BF_{24}NPRh$: C, 51.6; H, 3.6; N, 1.0. Found: C, 51.5; H, 3.8; N, 1.4.

Syn isomer: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.38 (d, 1 H, H_a), 7.32, 7.22, 7.03 (m, 4 H, H_b, H_e, H_d, H_f), 6.99 (m, 1 H, H_c), 3.61 (dd, 1 H, $^2J_{HH}$ = 14.3, $^2J_{HRh}$ = 3.0 Hz, RhC*H*H), 2.90 (dt, 1 H, $^2J_{HRh}$ = $^3J_{HP}$ = 2.7 Hz, RhCH*H*), 2.62, 1.53 (s, 3 H each, Me_β, Me_γ), 2.03 (s, 3 H, Me_α), 2.01 (d, 3 H, $^2J_{HP}$ = 8.3 Hz, PMe), 1.46 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5), 1.42 (br. s, 3 H, NH_3). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 153.6 (d, $^2J_{CP}$ = 33 Hz, C_1), 142.3, 140.11 (d, $^2J_{CP}$ = 9 Hz, C_4, C_6), 140.5 (C_3), 137.2 (dd, $^1J_{CP}$ = 54, $^2J_{CRh}$ = 2 Hz, C_2), 131.2 (CH_b, CH_e), 131.1, 130.7 (d, $^3J_{CP}$ = 8 Hz, CH_d, CH_f), 129.5 (d, $^3J_{CP}$ = 6 Hz, CH_c), 128.3 (d, $^1J_{CP}$ = 38 Hz, C_5), 127.9 (d, $^3J_{CP}$ = 17 Hz, CH_a), 99.0 (br. s, C_5Me_5), 34.0 (dd, $^1J_{CRh}$ = 23, $^3J_{CP}$ = 5 Hz, $RhCH_2$), 26.0, 23.3 (d, $^3J_{CP}$ = 6, $^3J_{CP}$ = 8 Hz, resp., Me_β, Me_γ), 20.4(d, $^3J_{CP}$ = 3 Hz, Me_α), 18.6 (d, $^1J_{CP}$ = 36 Hz, PMe), 8.52 (C_5Me_5).

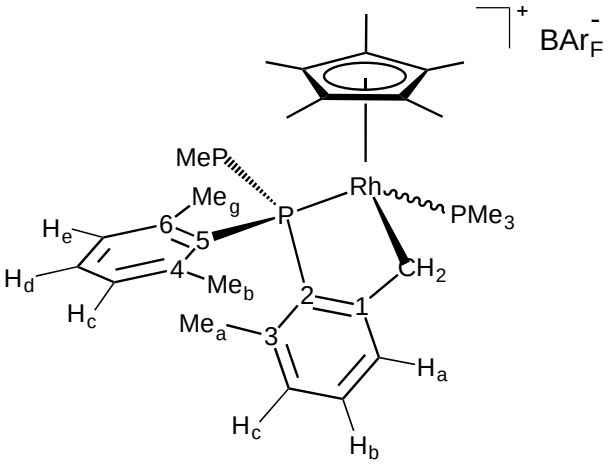
^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 34.0 (pseudo td, $^1J_{CH}$ = 135 Hz, $RhCH_2$).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 41.6 (d, $^1J_{PRh}$ = 150 Hz).

Anti isomer. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 3.21 (dt, 1 H, $^2J_{HH}$ = 11.6, $^2J_{HRh}$ = $^3J_{HP}$ = 2.9 Hz, RhC*H*H), 2.79 (dd, 1 H, $^2J_{HRh}$ = 2.4 Hz, RhCH*H*), 2.68, 1.76 (s, 3 H each, Me_β, Me_γ), 2.35 (s, 3 H, Me_α), 2.21 (d, 3 H, $^2J_{HP}$ = 9.5 Hz, PMe), 1.61 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5), 0.95 (br. s, 3 H, NH_3).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 38.3 (d, $^1J_{PRh}$ = 147 Hz).

(η^5-C_5Me_5)Rh(PMe$_3$){PMe(2,6-CH_2(Me)C_6H_3)(2,6-$Me_2C_6H_3$)} (3a·PMe$_3^+$)



Anal. Calc. for $C_{30}H_{44}F_6P_2RhSb$: C, 44.7; H, 5.5. Found: C, 44.4; H, 5.9.

Syn isomer: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) δ: 7.34-6.90 (m, 6 H, H_a, H_b, H_c, H_d, H_e, H_f), 3.16, 2.74 (m, 1 H each, $^2J_{HH}$ = 13.0, $^2J_{HRh}$ = 3.3 Hz, $RhCH_2$), 2.54, 1.39 (s, 3 H each, Me_β, Me_γ), 1.98 (s, 3 H, Me_α), 2.19 (d, 3 H, PMe), 1.53 (d, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5), 1.04 (s, 9 H, $^2J_{HP}$ = 9.7 Hz, PMe_3). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ºC) δ: 156.0 (d, $^2J_{CP}$ = 31 Hz, C_1), 142.2, 140.9 (d, $^2J_{CP}$ = 8 Hz, C_4, C_6), 140.8 (C_3), 136.4 (br.s, $^1J_{CP}$ = 54, C_2), 131.5, 130.7 (CH_b, CH_e), 130.9, 130.3 (d, $^3J_{CP}$ = 8 Hz, CH_d, CH_f), 129.7 (d, $^1J_{CP}$ = 35 Hz, C_5), 129.6 (d, $^3J_{CP}$ = 7 Hz, CH_c), 127.0 (d, $^3J_{CP}$ = 16 Hz, CH_a), 100.3 (br.s, C_5Me_5), 27.3 (ddd, $^1J_{CRh}$ = 23, $^2J_{CP}$ = 12, $^3J_{CP}$ = 3 Hz, $RhCH_2$), 26.5, 23.4 (d, $^3J_{CP}$ = 6, $^3J_{CP}$ = 8 Hz, resp., Me_β, Me_γ), 23.5 (d, $^1J_{CP}$ = 36 Hz, PMe), 21.0 (d, $^3J_{CP}$ = 3 Hz, Me_α), 17.3 (d, $^1J_{CP}$ = 32 Hz, PMe), 9.2 (C_5Me_5).

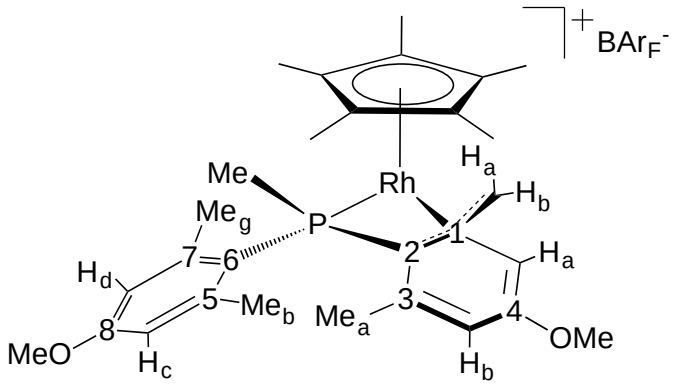
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 40.0 (dd, $^1J_{PRh}$ = 145 Hz, $^2J_{PP}$ = 45 Hz, PMe), 3.7 (dd, $^1J_{PRh}$ = 145 Hz, $^2J_{PP}$ = 45 Hz, PMe_3).

Anti isomer: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ºC) δ: 7.34-6.90 (m, 6 H, H_a, H_b, H_c, H_d, H_e, H_f), 3.16, 2.74 (m, 1 H each, $^2J_{HH}$ = 13.0, $^2J_{HRh}$ = 3.3 Hz, $RhCH_2$), 2.63, 1.79 (s, 3 H each, Me_β, Me_γ), 2.28 (s, 3 H, Me_α), 2.20 (d, 3 H, PMe), 1.69 (dd, 15 H, $^4J_{HP}$ = 2.5 Hz, C_5Me_5), 1.34 (s, 9 H, $^2J_{HP}$ = 9.7 Hz, PMe_3). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 25 ºC) δ: 158.6 (d, $^2J_{CP}$ = 33 Hz, C_1), 141.2, 140.3 (d, $^2J_{CP}$ = 12 Hz, C_4, C_6), 141.3 (C_3), 138.6 (dd, $^1J_{CP}$ = 51, C_2), 134.3 (d, $^1J_{CP}$ = 34 Hz, C_5), 131.7, 131.3 (d, $^3J_{CP}$ = 8 Hz, CH_d, CH_f), 131.2, 130.8 (CH_b, CH_e), 129.2 (d, $^3J_{CP}$ = 7 Hz, CH_c), 125.2 (d, $^3J_{CP}$ = 16 Hz, CH_a), 102.9 (br. s, C_5Me_5), 24.3, 23.6 (d, $^3J_{CP}$ = 10, $^3J_{CP}$ = 6 Hz, resp., Me_β, Me_γ), 23.5 (ddd, $^1J_{CRh}$ = 23, $^2J_{CP}$ = 9, $^3J_{CP}$ = 2 Hz, $RhCH_2$), 22.5 (br. s, Me_α), 19.0 (d, $^1J_{CP}$ = 32 Hz, PMe), 15.7 (d, $^1J_{CP}$ = 32 Hz, PMe), 10.0 (C_5Me_5).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: 28.0 (dd, $^1J_{PRh}$ = 145 Hz, $^2J_{PP}$ = 45 Hz, PMe), -2.59 (dd, $^1J_{PRh}$ = 145 Hz, $^2J_{PP}$ = 45 Hz, PMe_3).

[(η^5-C_5Me_5)Rh{PMe(κ^4-*P, C,C',C''*-2,6-CH_2(Me)-4-OMe-C_6H_2)(2,6-Me_2-4-OMe-C_6H_2)}]$^+$ $BArF^-$ (3c$^+$)



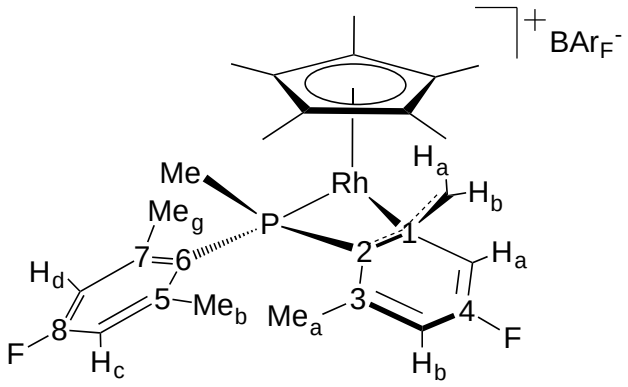
Anal. Calc. for $C_{61}H_{51}BF_{24}O_2PRh$**:** C, 51.7; H, 3.6. **Found:** C, 51.6; H, 3.9.

^{1}H NMR (400 MHz, 25 ºC, $CDCl_3$) δ: 7.18 (s, 1 H, H_b), 6.60 (s, 1 H, $H_{c/d}$), 6.47 (s, 1 H, $H_{d/c}$), 5.98 (s, 1 H, H_a), 3.71 (s, 6 H, OMe), 2.90 (d, 1 H, $^2J_{HH}$ = 4.3 Hz, $RhCH_\alpha$), 2.52 (s, 3 H, $Me_{\beta/\gamma}$), 2.43 (s, 3 H, Me_α), 2.10 (d, 3 H, $^2J_{HP}$ = 13.0 Hz, PMe), 2.00 (s, 3 H, $Me_{\gamma/\beta}$), 1.63 (d, 15 H, $^4J_{HP}$ = 2.8 Hz, C_5Me_5), 1.32 (dd, 1 H, $^3J_{HP}$ = 14.0, $^2J_{HH}$ = 3.6 Hz, $RhCH_\beta$).

^{13}C{^{1}H} NMR (100 MHz, 25 ºC, $CDCl_3$) δ: 163.6 (C_4, C_7), 144.0 ($C_{6,8}$), 143.2 (d, $^2J_{CP}$ = 21 Hz, $C_{6/8}$), 140.3 (C_3), 126.1 (d, $^3J_{CP}$ = 6 Hz, CH_b), 115.0 (d, $^3J_{CP}$ = 11 Hz, $CH_{c/d}$), 114.9 (d, $^3J_{CP}$ = 13 Hz, $CH_{c/d}$), 110.8 (d, $^1J_{CP}$ = 62 Hz, C_5), 108.5 (dd, $^1J_{CRh}$ = 14, $^2J_{CP}$ = 3 Hz, C_1), 100.2 (d, $^3J_{CP}$ = 8 Hz, CH_a), 98.6 (d, $^2J_{CP}$ = 6 Hz, C_5Me_5), 69.3 (d, $^1J_{CP}$ = 27 Hz, C_2), 55.2, 55.0 (Me_A, Me_B), 41.2 (d, $^2J_{CP}$ = 15 Hz, $RhCH_2$), 22.1, 21.9 (Me_α, $Me_{\beta/\gamma}$), 21.7 (d, $^3J_{CP}$ = 4 Hz, $Me_{\beta/\gamma}$), 13.4 (d, $^1J_{CP}$ = 34 Hz, PMe), 8.8 (C_5Me_5).

^{31}P{^{1}H} NMR (160 MHz, 25 ºC, $CDCl_3$) δ: - 17.5 (d, $^1J_{PRh}$ = 138 Hz).

[(η^5-C_5Me_5)Rh{PMe(κ^4-*P, C,C',C''*-2,6-CH_2(Me)-4-F-C_6H_2)(2,6-Me_2-4-F-C_6H_2)}]$^+$ $BArF^-$ ($3d^+$)



Anal. Calc. for $C_{59}H_{45}BF_{26}PRh$**:** C, 50.9; H, 3.3. **Found:** C, 50.9; H, 3.0.

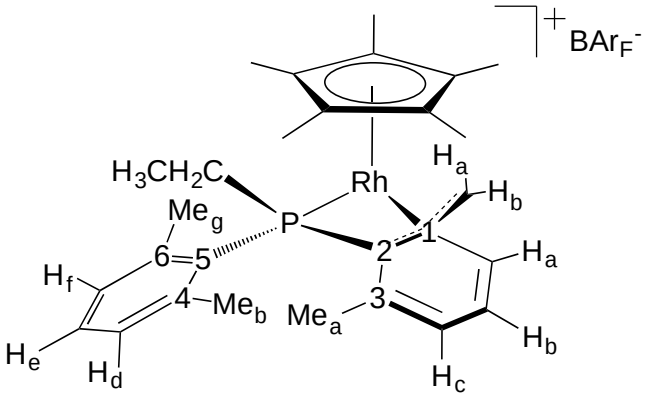
^{1}H NMR (400 MHz, 25 ºC, $CDCl_3$) δ: 7.31 (d, 1 H, $^3J_{HF}$ = 8.9 Hz, H_b), 6.81, 6.70 (br s, 2 H, H_c, H_d), 6.50 (d, 1 H, $^3J_{HF}$ = 8.6 Hz, H_a), 2.98 (d, 1 H, $^2J_{HH}$ = 4.7 Hz, $RhCH_\alpha$), 2.55, 2.01 (br s, 6 H, 2 $Me_{\beta/\gamma}$), 2.49 (s, 3 H, Me_α), 2.14 (d, 3 H, $^2J_{HP}$ = 12.8 Hz, PMe), 1.66 (d, 15 H, $^4J_{HP}$ = 2.9 Hz, C_5Me_5), 1.33 (dd, 1 H, $^3J_{HP}$ = 14.7, $^2J_{HH}$ = 4.7 Hz, $RhCH_\beta$).

^{13}C{^{1}H} NMR (100 MHz, 25 ºC, $CDCl_3$) δ: 165.5 (d, $^1J_{CF}$ = 259 Hz, $C_{4/7}$), 164.9 (d, $^1J_{CF}$ = 256 Hz, $C_{7/4}$), 145.6, 144.9 (br. s, C_6, C_8), 143.1 (d, $^3J_{CF}$ = 10 Hz, C_3), 123.7 (dd, $^2J_{CF}$ = 29 Hz, $^3J_{CP}$ = 6 Hz, CH_b), 117.4, 117.3 (dd, $^3J_{CP}$ = 10, $^2J_{CF}$ = 2 Hz, CH_c, CH_d), 115.8 (d, $^1J_{CP}$ = 60 Hz, C_5), 108.9 (dd, $^3J_{CP}$ = 8, $^2J_{CF}$ = 20 Hz, CH_a), 107.8 (C_1), 100.1 (d, $^2J_{CP}$ = 7 Hz, C_5Me_5), 73.5 (d, $^1J_{CP}$ = 25 Hz, C_2), 42.2 (d, $^2J_{CP}$ = 15 Hz, $RhCH_2$), 23.1 (Me_α), 22.2 (br. s, Me_β, Me_γ), 13.4 (d, $^1J_{CP}$ = 33 Hz, PMe), 9.4 (C_5Me_5).

^{31}P{^{1}H} NMR (160 MHz, 25 ºC, CD_2Cl_2) δ: - 16.4 (d, $^1J_{PRh}$ = 138 Hz).

^{19}F{^{1}H} NMR (160 MHz, 25 ºC, CD_2Cl_2) δ: - 103.7, - 107.0.

[(η^5-C_5Me_5)Rh{PEt(κ^4-*P, C,C',C''*-2,6-CH_2(Me)-C_6H_3)(Xyl)}]$^+$ $BArF^-$ (3e$^+$)



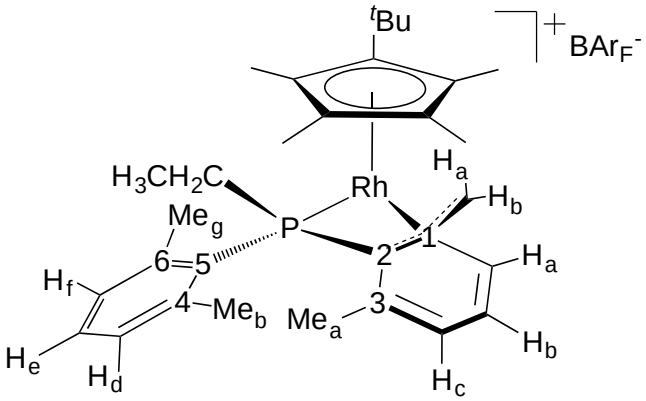
Anal. Calc. for $C_{60}H_{49}BF_{24}PRh$**:** C, 52.6; H, 3.6. **Found:** C, 52.3; H, 3.7.

^{1}H NMR (400 MHz, 25 ºC, CD_2Cl_2) δ: 7.55 (d, 1 H, $^3J_{HH}$ = 7.7 Hz, H_c), 7.46 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, H_b), 7.31 (t, 1 H, $^3J_{HH}$ = 7.6 Hz, H_e), 7.15 (t, 1 H, $^3J_{HH}$ = $^4J_{HP}$ = 6.9 Hz, $H_{d/f}$), 7.01 (d, 1 H, $^3J_{HH}$ = 6.2 Hz, $H_{f/d}$), 6.86 (dd, 1 H, $^3J_{HH}$ = 8.6, $^4J_{HP}$ = 3.3 Hz, H_a), 3.05 (d, 1 H, $^2J_{HH}$ = 4.1, $RhCH_\alpha$), 2.83 (m, 1H, $PCHHCH_3$), 2.64, 2.08 (s, 6 H, 2 $Me_{\beta/\gamma}$), 2.55 (s, 3 H, Me_α), 2.52 (m, 1 H, $PCHHCH_3$), 1.71 (d, 15 H, $^4J_{HP}$ = 2.8 Hz, C_5Me_5), 1.27 (dd, 1 H, $^2J_{HH}$ = 4.5, $^3J_{HP}$ = 13.8 Hz, $RhCH_\beta$), 1.27 (dt, 3 H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 21.9 Hz, PCH_2CH_3).

^{13}C{^{1}H} NMR (100 MHz, 25 ºC, CD_2Cl_2) δ: 143.4 ($C_{4/6}$), 143.1 (d, $^2J_{CP}$ = 18 Hz, $C_{6/4}$), 138.1 (C_3), 133.1 (CH_b), 132.7 (CH_c), 132.5 (d, $^3J_{CP}$ = 6 Hz, CH_c), 130.0 (d, $^3J_{CP}$ = 7 Hz, $CH_{d/f}$), 129.9 (d, $^3J_{CP}$ = 11 Hz, $CH_{f/d}$), 127.8 (d, $^3J_{CP}$ = 6 Hz, CH_a), 117.9 (d, $^1J_{CP}$ = 44 Hz, C_5), 104.4 (d, $^2J_{CP}$ = 12 Hz, C_1), 99.5 (d, $^3J_{CP}$ = 6 Hz, C_5Me_5), 77.9 (C_2), 42.6 (d, $^2J_{CP}$ = 14 Hz, $RhCH_2$), 23.2 (Me_α), 22.8 (d, $^3J_{CP}$ = 15 Hz, $Me_{\beta/\gamma}$), 22.3 (d, $^1J_{CP}$ = 30 Hz, PCH_2CH_3), 22.1 (d, $^3J_{CP}$ = 4 Hz, $Me_{\gamma/\beta}$), 9.4 (PCH_2CH_3), 9.4 (C_5Me_5).

^{31}P{^{1}H} NMR (160 MHz, 25 ºC, CD_2Cl_2) δ: -4.4 (d, $^1J_{PRh}$ = 135 Hz).

[(η^5-$C_5Me_4{}^tBu$)Rh{PMe(κ^4-*P, C,C',C''*-2,6-CH_2(Me)-C_6H_3)(Xyl)}]$^+$ $BArF^-$ (3f$^+$)



Anal. Calc. for $C_{30}H_{41}F_6PRhSb$: C, 46.7; H, 5.4. **Found:** C, 47.0; H, 5.6.

EM (ES) m/z Calc for M+ ($C_{30}H_{41}RhP$): 535.20. **Found:** 535.20.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 ºC) δ: 7.58 (m, 1 H, H_c), 7.52 (m, 1 H, H_b), 7.30 (td, 1 H, $^5J_{HP}$ = 1.5 Hz, H_e), 7.15, 6.97 (m, 1 H each, H_d, H_f), 6.94 (dd, 1 H, $^4J_{HP}$ = 3.5, H_a), 3.34 (dt, 1 H, $^2J_{HH}$ = 4.5, $^2J_{HRh}$ = $^3J_{HP}$ = 1.5 Hz, $RhCH_\alpha$), 2.67, 2.02 (s, 3 H each, Me_β, Me_γ), 2.64 (s, 3 H, Me_α), 2.30 (d, 3 H, $^2J_{HP}$ = 12.7 Hz, PMe), 1.93, 1.42 (d, 3 H each, $^4J_{HP}$ = 2.5 Hz, Me_c, Me_d), 1.92, 1.80 (d, 3 H each, $^4J_{HP}$ = 4.0 Hz, Me_a, Me_b), 1.37 (ddd, 1 H, $^3J_{HP}$ = 10.0, $^2J_{HRh}$ = 1.5 Hz, $RhCH_\beta$), 1.31 (s, 9 H, ^{t}Bu). All aromatic couplings are of *ca.* $^3J_{HH} \approx 7.5$ Hz.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 142.7, 142.0 (s, d, $^2J_{CP}$ = 18 Hz, resp., C_4, C_6), 138.7 (C_3), 133.5 (CH_b), 133.4 (CH_c), 132.4 (CH_e), 129.9, 129.7 (d, $^3J_{CP}$ = 8 Hz, CH_d, CH_f), 128.4 (d, $^3J_{CP}$ = 6 Hz, CH_a), 121.7 (d, $^1J_{CP}$ = 55 Hz, C_5), 114.3 (dd, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, $C_q{}^t$Bu), 104.2 (dd, $^2J_{CP}$ = 14, $^1J_{CRh}$ = 4 Hz, C_1), 100.0, 100.4, 99.8, 98.0 (dd, $^1J_{CRh}$ = $^2J_{CP}$ = 3 Hz, C_qMe$_a$, C_qMe$_b$, C_qMe$_c$, C_qMe$_d$), 79.4 (dd, $^1J_{CP}$ = 24, $^1J_{CRh}$ = 2 Hz, C_2), 40.4 (dd, $^1J_{CRh}$ = 14, $^2J_{CP}$ = 2 Hz, $RhCH_2$), 34.2 (CMe$_3$), 32.11 (^{t}Bu), 23.2 (Me_α), 22.5, 22.1 (d, s, $^3J_{CP}$ = 18 Hz, resp., Me_β, Me_γ), 13.7 (d, $^1J_{CP}$ = 32 Hz, PMe), 13.4, 8.8 (Me_a, Me_b), 12.7, 10.5 (Me_c, Me_d).

^{13}C NMR (100 MHz, CD_2Cl_2, 25 ºC) δ: 40.4 (pseudo td, $^1J_{CH}$ = 158, Hz, $RhCH_2$).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 ºC) δ: -15.5 (d, $^1J_{PRh}$ = 138 Hz).

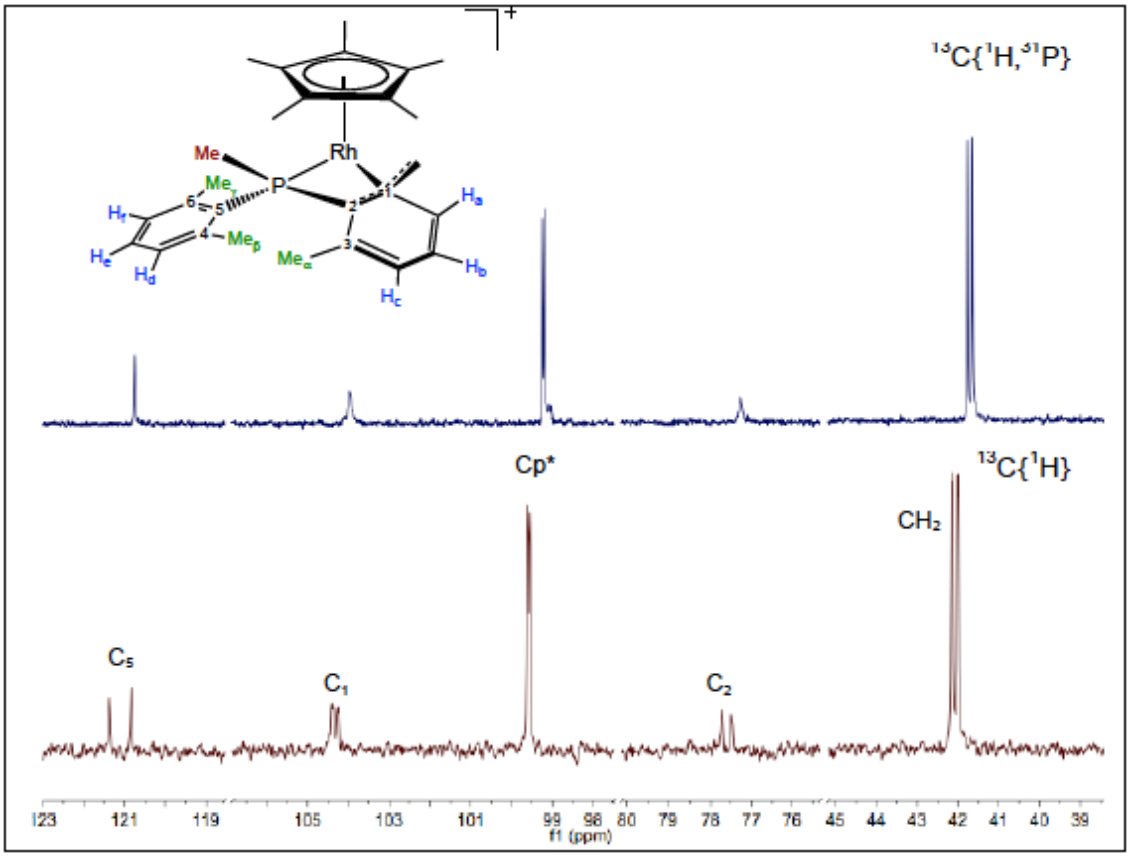


Figure S2. $^{13}C\{^1H\}$ and ^{13}C NMR spectrum of **3a**$^+$.

3. Low temperature reaction of 3$^+$ with H_2.

A Young NMR tube was charged with **3b**$^+$-**3e**$^+$ (7.4·10-3 mmol) and CD_2Cl_2 (0.5 mL), then degassed via three freeze-thaw cycles. The tube was charged with H_2 (2 bar) and vigorously shaken. The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR. No reaction was observed at this temperature, so the probe was cooled down from 25 ºC to -90 ºC. The corresponding agostic hydride **4**$^+$ could only be detected between -70 ºC and -90 ºC (except in the case of **3c**$^+$, where no signs of the corresponding **4c**$^+$ were recorded). When the NMR tube was warmed up to 25 ºC NMR signals of the agostic species disappeared. They were, however, restored upon cooling again at -80 ºC. The same results were obtained when the NMR tube was charged with H_2 at -80 ºC and placed in a pre-cooled NMR probe (-80 ºC).

4. Spectroscopic data of agostic hydrides 4$^+$

The agostic species **4**$^+$ could not be completely characterized by NMR spectroscopy due to the very low **4**$^+$:**3**$^+$ ratio at -80 ºC, along with the fact that many ^1H NMR resonances due to minor compound **4**$^+$ overlap with those resulting from **3**$^+$. A selection of relevant NMR data is collected bellow. For complex **4a**$^+$ the $^{13}C\{^1H\}$ NMR assignment for the agostic methyl group was derived from ^1H-^{13}C two-dimensional NMR spectroscopic analysis. The intramolecular chemical exchange between the hydrides and the agostic methyl groups was proved by 2D-EXSY at -80 ºC.

4a^{+}: **^{1}H NMR** (400 MHz, CD_2Cl_2, -80 ºC) δ: 2.23 (d, 3 H, $^{1}J_{HP}$ = 9.0 Hz, PMe), 1.71 (C_5Me_5, overlapped with **3a**$^{+}$-C_5Me_5), 0.02 (br. s, 3 H, agostic Rh··CH_3), -9.43 (dd, 1 H, $^{1}J_{HRh}$ = 18.5, $^{1}J_{HP}$ = 37 Hz, Rh-H).

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, -80 ºC) δ: -5.4 (agostic Rh··CH_3).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, -80 ºC) δ: 29.8 (d, $^{1}J_{PRh}$ = 138 Hz).

4b^{+}: **^{1}H NMR** (400 MHz, CD_2Cl_2, -80 ºC) δ: 2.22 (br. d, 3 H, $^{1}J_{HP}$ = 9.1 Hz, PMe), 1.52 (C_5Me_5, overlapped with **3b**$^{+}$-C_5Me_5), -0.03 (br. s, 3 H, agostic Rh··CH_3), -9.48 (br. s, Rh-H).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, -80 ºC) δ: 28.6 (d, $^{1}J_{PRh}$ = 139 Hz).

4d^{+}: **^{1}H NMR** (400 MHz, CD_2Cl_2, -80 ºC) δ: 2.23 (d, 3 H, $^{1}J_{HP}$ = 9.6 Hz, PMe), 1.66 (C_5Me_5, overlapped with **3d**$^{+}$-C_5Me_5), 0.02 (br. s, 3 H, agostic Rh··CH_3), -9.23 (br. s, 1 H, Rh-H).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, -80 ºC) δ: 27.6 (d, $^{1}J_{PRh}$ = 141 Hz).

4e^{+}: **^{1}H NMR** (400 MHz, CD_2Cl_2, -80 ºC) δ: 2.26 (br. s, 3 H, PMe), 1.48 (C_5Me_5, overlapped with **3e**$^{+}$-C_5Me_5), -0.15 (br. s, 3 H, agostic Rh··CH_3), -9.38 (br. s, 1 H, Rh-H).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, -80 ºC) δ: 46.9 (d, $^{1}J_{PRh}$ = 136 Hz).

5. General procedure for Si–H/Si–D exchanges.

The screening of all the silanes tested for deuteration was undertaken at low scale without further purification of the deuterated organosilanes. The corresponding catalyst **3**$^{+}$ (2.2·10-3 mmol) and the hydrosilane (0.22 mmol) were dissolved in CD_2Cl_2 (0.6 mL) in a Young ampoule (volume *ca.* 50 mL). The solution was cooled to 0 ºC and the argon pumped out and replaced by deuterium (0.5 bar). The solution was stirred vigorously at room temperature for 3 hours (although it has been observed that H/D exchange is completed at lower times) and deuterium incorporation determined by IR and ^{1}H-NMR spectroscopy. Under these conditions only one or two D_2 loading were enough to label the Si–H bond at yields higher than 99%. For experiments with lower amounts of catalyst and/or higher amounts of silane three cycles of 0 ºC/vacuum (≈0.1 bar, 20 s)/fresh D_2 were routinely employed.

6. General method for the hydrosilylation of C-O multiple bonds.

In a typical experiment, a 2 mL screw-cap glass vial was charged with the corresponding catalyst **3**$^{+}$ (0.5·10-3 mmol), the hydrosilane (1.1 mmol), the organic substrate (0.5 mmol) and CD_2Cl_2 (0.5 mL) in a glovebox. After stirring for 1 hour, the reaction mixture was transferred to a screw-cap NMR tube and the reaction progress checked by ^{1}H-NMR spectroscopy.

7. Kinetic studies.

The corresponding amounts of triethylsilane and acetophenone were added to a Young NMR tube under argon and dissolved in CD_2Cl_2 (0.5 mL). Catalyst **3**$^{+}$ was then added as a stock solution in CD_2Cl_2 (100 µL, $8.4x10^{-4}$ M) and the reaction immediately monitored by ^{1}H NMR spectroscopy using hexamethylbenzene as internal standard.

8. X-Ray structure analysis.

A single crystal of suitable size, coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173(2) K] to the goniometer head. Data collection was performed on Bruker-Nonius X8APEX-II CCD diffractometer, using monochromatic radiation λ(Mo $K_{\alpha 1}$) = 0.71073 Å, by means of ω and φ scans. The data were reduced (SAINT)[3] and corrected for Lorentz polarization effects and absorption by multiscan method applied by SADABS.[4] The structure was solved by direct methods (SIR-2002)[5] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12).[6] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. CCDC-1566023 (**2a**), 1566027 (**2b**), 1566025 (**2g**), 1566024 (**3d**$^+$), 1566028 (**3e**$^+$), 1566026 (**3f**$^+$), 783589 (**3a·CO**$^+$), 1571395 (**3a·NCCH$_3$**$^+$) and 1571397 (**3a·C$_2$H$_4$**$^+$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure 2 collects ORTEP perspective views of the molecular structures of complexes **2b** and **2g**. Metrical parameters have normal values, with average Rh—C, Rh—Cl and Rh—P bond distances of 2.096, 2.350 and 2.252 Å, respectively. The C-Rh-P bond angles within the metalated moiety have values close to 82º, that do not deviate appreciably from the ideal 90º value expected for a pseudo octahedral structure.

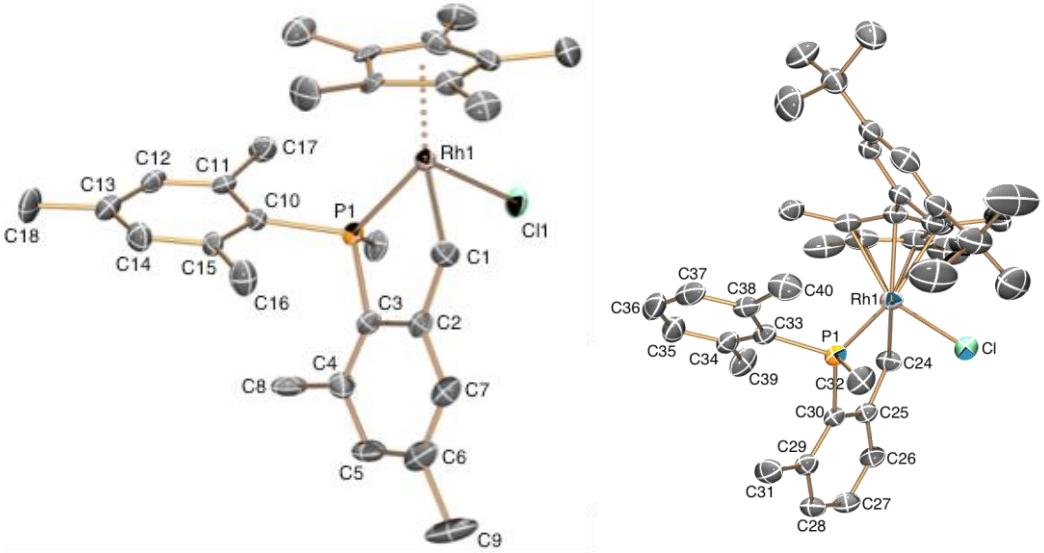


Figure S3. The solid-state molecular structure of complexes **2b** (left) and **2g** (right); hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 50%. Selected bond distances (Å) and angles (º) for **2b**: Rh1—Cl1 = 2.397(2); Rh1—P1 = 2.251(2); Rh1—C1 = 2.101(8); C1—C2 = 1.49(1); C2—C3 = 1.41(1); C3—C4 = 1.40(1); C4—C5 = 1.41(1); C5—C6 = 1.41(1); C6—C7 = 1.37(1); C7—C2 = 1.39(1); C2-C1-Rh1 = 117.5(5); C1-C2-C3 = 119.7(7); C1-Rh1-Cl1 = 86.2(3); C2-C3-P1 = 111.4(6); C1-Rh1-P1 = 82.1(2); P1-Rh1-Cl1 = 87.25(8). Selected bond distances (Å) and angles (º) for **2g**: Rh1—Cl = 2.382(1); Rh1—P1 = 2.250(1); Rh1—C24 = 2.086(2); C24—C25 = 1.494(2); C25—C30 = 1.399(2); C30—C29 = 1.405(2); C29—C28 = 1.383(2); C28—C27 = 1.386(3); C27—C26 = 1.374(3); C26—C25 = 1.397(2); C25-C24-Rh1 =

117.3(1); C24-C25-C30 = 120.2(2); C24-Rh1-Cl = 85.28(6); C25-C30-P1 = 112.0(1); C24-Rh1-P1 = 82.71(6); P1-Rh1-Cl = 88.62(2).

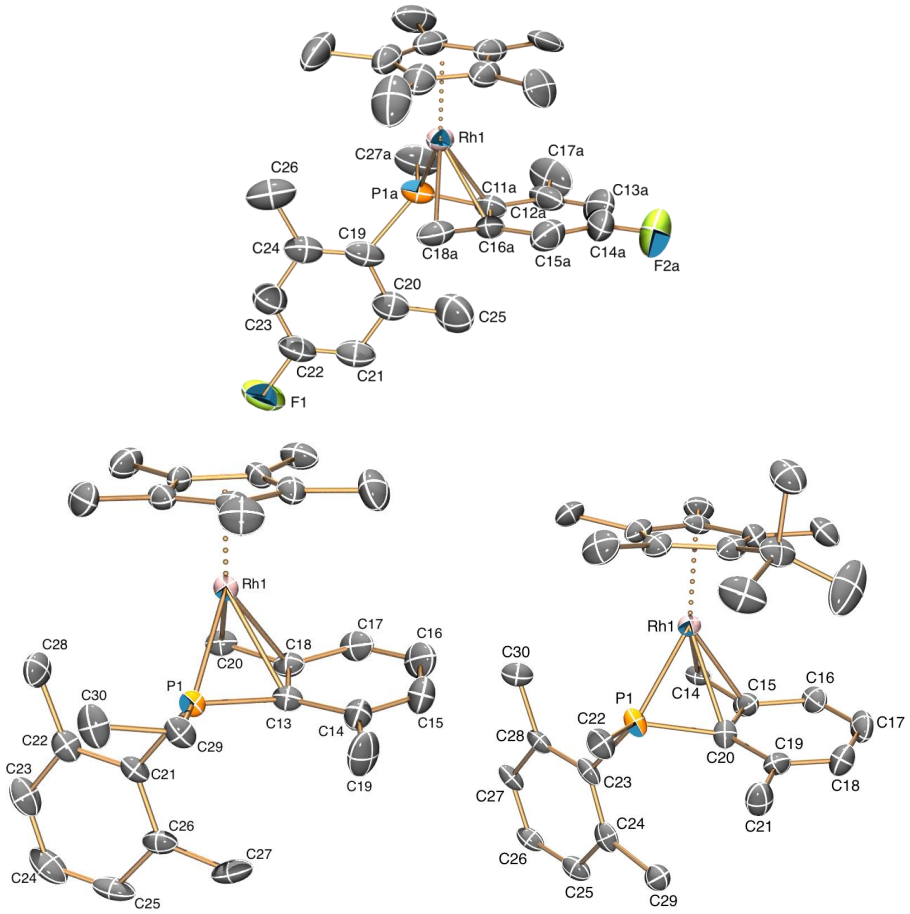


Figure S4. ORTEP perspective views of the molecules of **3d**$^{+}$ (top), **3e**$^{+}$ (left) and **3f**$^{+}$ (right); hydrogen atoms are excluded for clarity and thermal ellipsoids are set at 50%. Selected bond distances (Å) and angles (º) for **3d**$^{+}$: Rh1—P1a = 2.27(1); Rh1—C11a = 2.25(1); Rh1—C16a = 2.22(1); Rh1—C18a = 2.25(2); C11a—C16a = 1.43(1); C16a—C18a = 1.43(2); P1a—C11a = 1.79(1); C11a-C16a-C18a = 126(1); P1a-C11a-C16a = 111.9(8). Selected bond distances (Å) and angles (º) for **3e**$^{+}$: Rh1—P1 = 2.257(1); Rh1—C13 = 2.289(5); Rh1—C18 = 2.220(5); Rh1—C20 = 2.141(5); C17—C18 = 1.428(8); C16—C17 = 1.347(9); C15—C16 = 1.416(9); C14—C15 = 1.355(8); C13—14 = 1.439(8); C13—C18 = 1.449(7); C18—C20 = 1.446(8); P1—C13 = 1.815(6); C13-C18-C20 = 118.4(5); P1-C13-C18 = 110.7(4). Selected bond distances (Å) and angles (º) for **3f**$^{+}$: Rh1—P1 = 2.254(3); Rh—C14 = 2.1449(9); Rh1—C15 = 2.219(9); Rh1—C20 = 2.271(9); C14—C15 = 1.451(13); C15—C20 = 1.454(12); P1—C20 = 1.795(9); C19—C20 = 1.445(13); C15—C16 = 1.433(13); C16—C17 = 1.355(15); C17—C18 = 1.409(16); C18—C19 = 1.379(15); C14-C15-C20 = 117.8(8); C15-C20-P1 = 111.0(6).

8.1. X-Ray structure analysis of 2a.

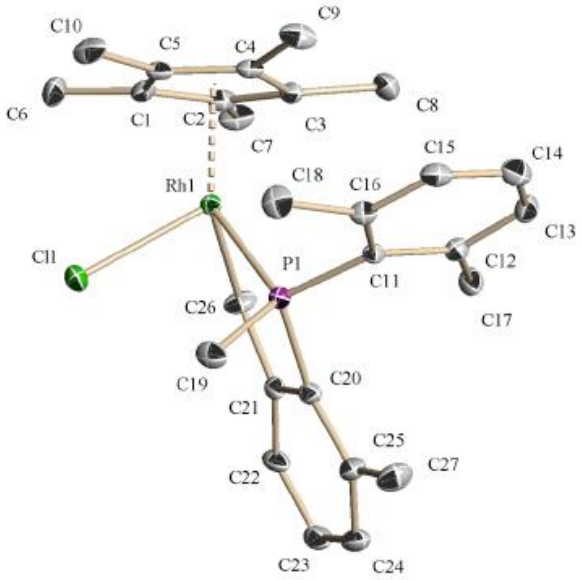


Figure S5. X–ray molecular structure of **2a**, with H atoms omitted for clarity.

Table S1. Crystal data and structure refinement for **2a**.

Empirical formula	$C_{27}H_{35}ClPRh$
Formula weight	528.88
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 8.2270(7) Å α = 90º b = 8.5008(7) Å β = 91.944(2)º c = 17.1978 Å γ = 90º
Volume	1202.06(17)Å^3
Z	2
Density (calculated)	1.461 Mg/mm^{-3}
Absorption coefficient	0.900 mm^{-1}
F(000)	548.0
Crystal size	0.10 × 0.08 × 0.08 mm^3
Theta range for data collection	2.36 to 60.98°
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 11, -24 ≤ l ≤ 21
Reflections collected	15134
Independent reflections	6072 [R(int) = 0.0408]
Completeness to theta = 25.25°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.917 and 0.931
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6203/0/280
Goodness-of-fit on F^2	0.999
Final R indexes [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0753
Final R indexes [all data]	R1 = 0.0482, wR2 = 0.0795
Largest diff. Peak and hole	0.84 and -0.85 e· Å^{-3}

Table S2. Selected bond lengths [Å] and angles [°] for **2a**.

Bond Distances			
Rh-P(1)	2.2550(10)	P(1)-C(19)	1.834(4)
Rh-Cl(1)	2.3895(10)	P(1)-C(20)	1.821(4)
Rh-C(26)	2.101(3)	C(24)-C(25)	1.494(2)
Rh-C(1)	2.221(3)	C(24)-C(30)	1.399(2)
Rh-C(2)	2.228(4)	C(20)-C(21)	1.391(5)
Rh-C(3)	2.178(3)	C(21)-C(22)	1.402(5)
Rh-C(4)	2.268(3)	C(22)-C(23)	1.385(6)
Rh-C(5)	2.250(4)	C(23)-C(24)	1.391(7)
P(1)-C(11)	1.833(4)	C(24)-C(25)	1.389(6)

Bond Angles (º)			
C(26)-Rh-P(1)	81.44(11)	C(20)-P(1)-Rh	106.87(13)
C(26)-Rh-Cl(1)	87.88(12)	C(20)-P(1)-C(11)	111.03(17)
C(11)-P(1)-Rh	115.75(11)	C(11)-P(1)-C(19)	107.41(18)
P(1)-Rh-Cl(1)	90.05(4)	C(20)-P(1)-C(19)	98.11(18)
C(19)-P(1)-Rh	116.26(16)		

8.2. X-Ray structure analysis of 2b.

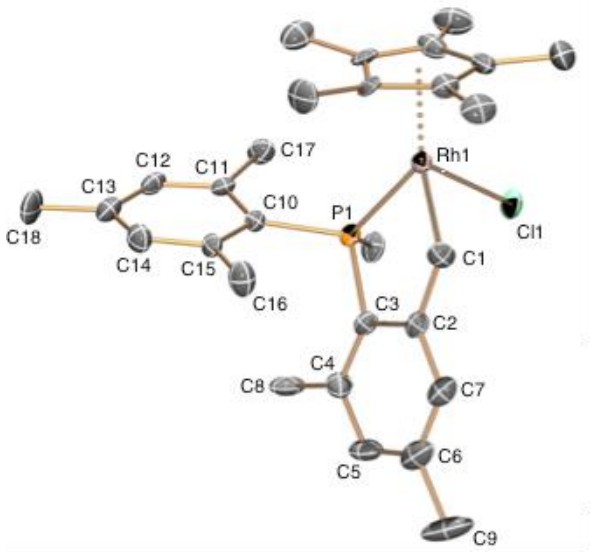


Figure S6. X–ray molecular structure of **2b**, with H atoms omitted for clarity.

Table S3. Crystal data and structure refinement for **2b**.

Empirical formula	$C_{29}H_{39}ClPRh$	
Formula weight	556.97	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 8.7455(2) Å	α = 90º
	b = 8.5799(2) Å	β = 89.9780(10)º
	c = 35.2320(8) Å	γ = 90º
Volume	2643.65(11) $Å^3$	
Z	4	
Density (calculated)	1.399 Mg/mm^{-3}	
Absorption coefficient	0.822 mm^{-1}	
F(000)	1160.0	
Crystal size	0.17 × 0.13 × 0.09 mm^3	
Theta range for data collection	2.32 to 55.64°	
Index ranges	$11 \leq h \leq 11$, $11 \leq k \leq 11$, $46 \leq l \leq 42$	
Reflections collected	32535	
Independent reflections	6203 [R(int) = 0.0463]	
Completeness to theta = 25.25°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.894 and 0.766	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6203/0/289	
Goodness-of-fit on F^2	1.314	
Final R indexes [I>2sigma(I)]	R1 = 0.0642, wR2 = 0.1702	
Final R indexes [all data]	R1 = 0.0674, wR2 = 0.1765	
Largest diff. Peak and hole	2.16 and -2.16 e· $Å^{-3}$	

Table S4. Selected bond lengths [Å] and angles [°] for **2b**.

Bond Distances			
Rh1—Cl1	2.397(2)	C2—C3	1.41(1)
Rh1—P1	2.251(2)	C3—C4	1.40(1)
Rh1—C1	2.101(8)	C4—C5	1.41(1)
C1—C2	1.49(1)	C5—C6	1.41(1)
C6—C7	1.37(1)	C7—C2	1.39(1)

Bond Angles (º)			
C2-C1-Rh1	117.5(5)	C1-C2-C3	119.7(7)
C1-Rh1-Cl1	86.2(3)	C2-C3-P1	111.4(6)
C1-Rh1-P1	82.1(2)	P1-Rh1-Cl1	87.25(8)

8.3. X-Ray structure analysis of 2g.

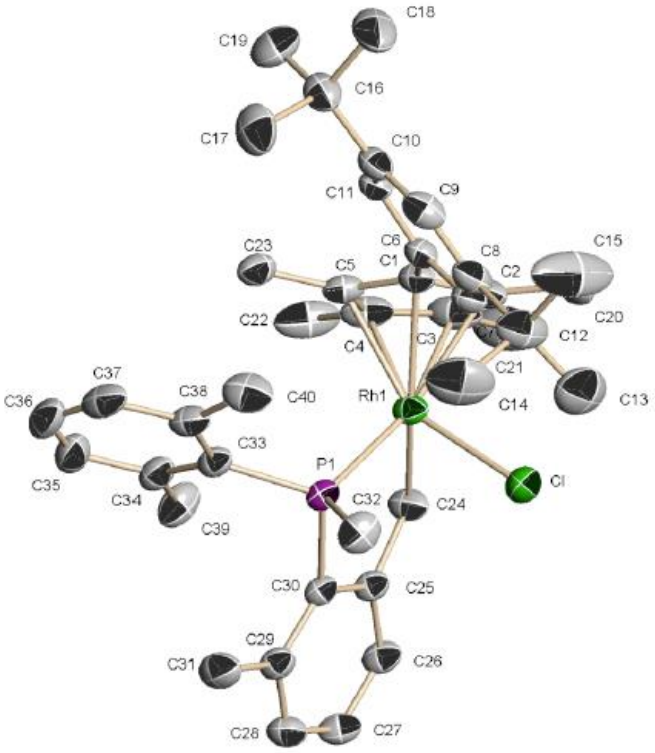


Figure S7. X–ray molecular structure of **2g**, with H atoms omitted for clarity.

Table S5. Crystal data and structure refinement for **2g**.

Empirical formula	$C_{45}H_{65}ClPRh$
Formula weight	775.30
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 16.1565(4) Å α□ □ □90º b = 16.6787(4) Å β = 101.8650(10)º c = 16.0638(4) Å γ = 90º
Volume	4236.22(18) $Å^3$
Z	4
Density (calculated)	1.216 Mg/mm^{-3}
Absorption coefficient	2.398 mm^{-1}
F(000)	1648
Crystal size	0.28 × 0.23 × 0.21 mm^3
Theta range for data collection	2.35 to 30.51°
Index ranges	$-23 \le h \le 23, -23 \le k \le 20, -22 \le l \le 22$
Reflections collected	89457
Independent reflections	12863 [R(int) = 0.0317]
Completeness to theta = 25.25°	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.894 and 0.766

Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12863 / 0 / 463
Goodness-of-fit on F^2	1.028
Final R indexes [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0885
Final R indexes [all data]	R1 = 0.0517, wR2 = 0.0977
Largest diff. Peak and hole	1.040 and -1.131 e· $Å^{-3}$

Table S6. Selected bond lengths [Å] and angles [°] for **2g**.

Bond Distances			
Rh-P(1)	2.2499(5)	Rh-C(5)	2.2265(18)
Rh-Cl	2.2647(17)	P(1)-C(30)	1.8139(17)
Rh-C(24)	2.0856(18)	P(1)-C(32)	1.8282(19)
Rh-C(1)	2.2647(17)	P(1)-C(33)	1.8342(18)
Rh-C(2)	2.2406(19)	C(24)-C(25)	C(24)-C(25)
Rh-C(3)	2.210(2)	C(24)-C(30)	1.399(2)
Rh-C(4)	2.181(2)		

Bond Angles (º)			
C(24)-Rh-P(1)	82.71(5)	C(33)-P(1)-Rh	118.64(6)
C(24)-Rh-Cl	85.28(6)	C(30)-P(1)-C(32)	107.60(5)
P(1)-Rh-Cl	88.623(19)	C(30)-P(1)-C(33)	107.53(8)
C(30)-P(1)-Rh	106.65(9)	C(32)-P(1)-C(33)	106.65(9)
C(32)-P(1)-Rh	115.32(8)		

8.4. X-Ray structure analysis of $3d^+$.

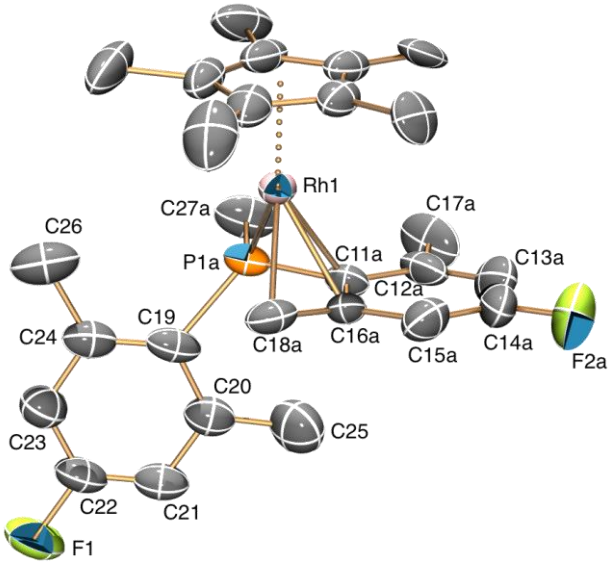


Figure S8. X–ray molecular structure of $\mathbf{3d^+}$, with H atoms and BAr_F^- omitted for clarity.

Table S7. Crystal data and structure refinement for **3d**$^{+}$.

Empirical formula	$C_{59}H_{45}BF_{26}PRh$
Formula weight	1392.64
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 (1)/c
Unit cell dimensions	a = 12.5042(3) Å α = 90º b = 19.0743(5) Å β = 97.7430(10)º c = 24.8642(7) Å γ = 90º
Volume	5876.3(3) Å^3
Z	4
Density (calculated)	1.574 Mg/mm^{-3}
Absorption coefficient	0.439 mm^{-1}
F(000)	2792.0
Crystal size	0.2 × 0.18 × 0.13 mm^3
Theta range for data collection	2.7 to 50.5°
Index ranges	$15 \leq h \leq 14$, $22 \leq k \leq 22$, $29 \leq l \leq 27$
Reflections collected	83676
Independent reflections	10632 [R(int) = 0.0306]
Completeness to theta = 25.25°	100 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.916 and 0.945
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10632/256/860
Goodness-of-fit on F^2	1.102
Final R indexes [I>2sigma(I)]	R1 = 0.0828, wR2 = 0.2384
Final R indexes [all data]	R1 = 0.1001, wR2 = 0.2543
Largest diff. Peak and hole	1.85 and -1.31 e· Å^{-3}

Table S8. Selected bond lengths [Å] and angles [°] for **3d**$^{+}$.

Bond Distances			
Rh1a—P1a	2.269(7)	Rh1a—C11a	2.252(9)
Rh1a—C16a	2.220(8)	Rh1a—C18a	2.24(1)
C11a—C12a	1.44(1)	C12a—C13a	1.34(2)
C13a—C14a	1.46(2)	C14a—C15a	1.33(2)
C15a—C16a	1.42(1)	C11a—C16a	1.44(1)
C16a—C18a	1.43(2)	P1a—C11a	1.79(1)
Bond Angles (º)			
C11a-C16a-C18a	124.7(1)	P1a-C11a-C16a	111.9(7)

8.5. X-Ray structure analysis of $3e^+$.

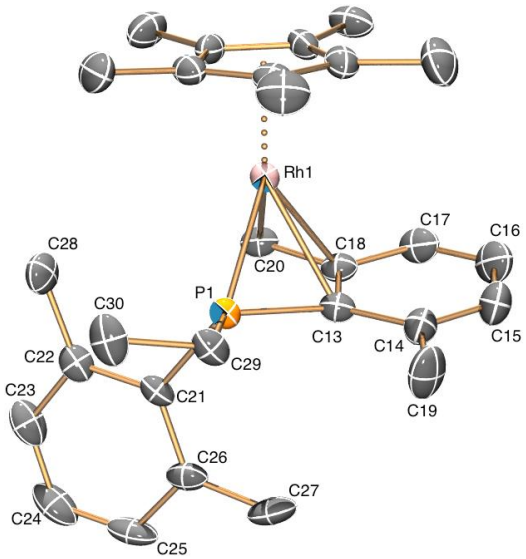


Figure S8. X–ray molecular structure of **3e**$^+$, with H atoms and SbF_6^- omitted for clarity.

Table S9. Crystal data and structure refinement for **3e**$^+$.

Empirical formula	$C_{28}H_{37}F_6PRhSb$
Formula weight	743.21
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 (1)/c
Unit cell dimensions	a = 8.7806(3) Å α = 90º b = 30.0574(12) Å β = 100.328(2)º c = 11.2403(4) Å γ = 90º
Volume	2918.50(19) $Å^3$
Z	4
Density (calculated)	1.691 Mg/mm^{-3}
Absorption coefficient	1.600 mm^{-1}
F(000)	1480.0
Crystal size	0.25 × 0.2 × 0.14 mm^3
Theta range for data collection	2.7 to 50.5°
Index ranges	$10 \leq h \leq 10$, $29 \leq k \leq 36$, $13 \leq l \leq 13$
Reflections collected	29887
Independent reflections	5210 [R(int) = 0.0278]
Completeness to theta = 25.25°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.688 and 0.799
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5210/338/353
Goodness-of-fit on F^2	1.290
Final R indexes [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.0869
Final R indexes [all data]	R1 = 0.0519, wR2 = 0.0897
Largest diff. Peak and hole	1.56 and 1.22 e· $Å^{-3}$

Table S10. Selected bond lengths [Å] and angles [°] for **3e**$^{+}$.

Bond Distances			
Rh1—P1	2.257(1)	Rh1—C13	2.289(5)
Rh1—C18	2.220(5)	Rh1—C20	2.141(5)
C17—C18	1.428(8)	C16—C17	1.347(9)
C15—C16	1.416(9)	C14—C15	1.355(8)
C13—14	1.439(8)	C13—C18	1.449(7)
C18—C20	1.446(8)	P1—C13	1.815(6)
Bond Angles (º)			
C13-C18-C20	118.4(5)	P1-C13-C18	110.7(4)

8.6. X-Ray structure analysis of 3f^{+}.

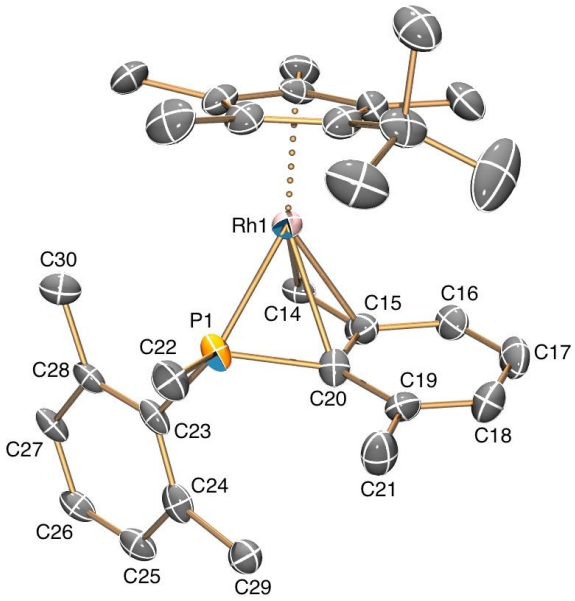


Figure S9 X–ray molecular structure of **3f**$^{+}$, with H atoms and SbF_6^- omitted for clarity.

Table S11. Crystal data and structure refinement for **3f**$^+$.

Empirical formula	$C_{30}H_{41}F_6PRhSb$
Formula weight	771.26
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.4942(8) Å α = 86.453(1)º b = 13.9801(8) Å β = 80.876(1)º c = 18.2211(11)Å γ = 88.840(1)º
Volume	3136.2(3)Å^3
Z	4
Density (calculated)	1.633 Mg/mm^{-3}
Absorption coefficient	1.492 mm^{-1}
F(000)	1544.0
Crystal size	0.34 × 0.28 × 0.15 mm^3
Theta range for data collection	2.92 to 61.08°
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 19, -25 ≤ l ≤ 26
Reflections collected	106633
Independent reflections	18303 [R(int) = 0.0290]
Completeness to theta = 25.25°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6119 and 0.8012
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	18303/0/725
Goodness-of-fit on F^2	1.308
Final R indexes [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1578
Final R indexes [all data]	R1 = 0.0764, wR2 = 0.1882
Largest diff. Peak and hole	6.53 and -4.72 e$^-$ Å^{-3}

Table S12. Selected bond lengths [Å] and angles [°] for **3f**$^+$.

Bond Distances			
Rh-P(1)	2.254(3)	P(1)-C(22)	1.812(10)
Rh-C(14)	2.1449(9)	P(1)-C(23)	1.831(10)
Rh-C(15)	2.219(9)	C(15)-C(16)	1.433(13)
Rh-C(20)	2.271(9)	C(16)-C(17)	1.355(15)
Rh-C(1)	2.189(8)	C(17)-C(18)	1.409(16)
Rh-C(3)	2.223(9)	C(19)-C(20)	1.445(13)
Rh-C(4)	2.230(9)	C(15)-C(20)	1.454(12)
Rh-C(5)	2.186(8)	C(19)-C(21)	1.505(14)
P(1)-C(20)	1.795(9)	C(23)-C(28)	1.414(15)
Rh-C(2)	2.198(8)	C(18)-C(19)	1.379(15)
C(14)-C(15)	1.451(13)		

Bond Angles (º)			
C(14)-Rh-C(15)	38.8(3)	C(19)-C(20)-P(1)	129.6(7)
C(15)-Rh-C(20)	37.8(3)	C(15)-C(20)-Rh	69.2(5)
C(20)-Rh-P(1)	46.6(2)	P(1)-C(20)-Rh	66.4(3)
C(14)-Rh-C(20)	68.6(3)	C(19)-C(20)-Rh	123.7(6)

8.7. X-Ray structure analysis of 3a·CO$^+$.

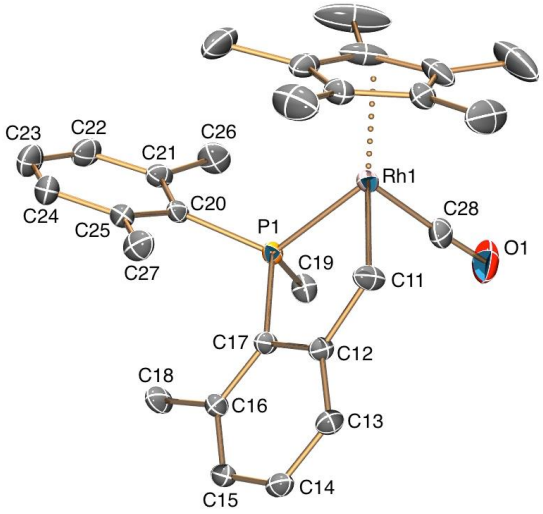


Figure S10. X–ray molecular structure of **3a·CO$^+$**, with H atoms and BAr_F^- omitted for clarity.

Table S13. Crystal data and structure refinement for **3a·CO$^+$**.

Empirical formula	$C_{60}H_{47}BF_{24}OPRh$	
Formula weight	1384.67	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.1421(3) Å	α = 89.147(2)°
	b = 12.9364(3) Å	β = 72.1240(10)°
	c = 19.6945(6) Å	γ = 86.3190(10)°
Volume	2938.06(13) Å^3	
Z	2	
Density (calculated)	1.565 Mg/mm^{-3}	
Absorption coefficient	0.435 mm^{-1}	
F(000)	1392.0	
Crystal size	0.28 × 0.21 × 0.13 mm^3	
Theta range for data collection	2.18 to 66.28°	
Index ranges	$-18 \le h \le 18$, $-19 \le k \le 19$, $-30 \le l \le 30$	
Reflections collected	80405	
Independent reflections	21936 [R(int) = 0.0270]	
Completeness to theta = 25.25°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.945 and 0.754	

Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	21936/0/829
Goodness-of-fit on F^2	1.050
Final R indexes [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1164
Final R indexes [all data]	R1 = 0.0593, wR2 = 0.1273
Largest diff. Peak and hole	2.12 and -1.41 e^- $Å^{-3}$

Table S14. Selected bond lengths [Å] and angles [°] for **3·CO**$^+$.

Bond Distances			
Rh(1) —C(28)	1.879(2)	P(1)—C(17)	1.815(2)
Rh(1)—C(11)	2.124(2)	C(12)—C(13)	1.404(3)
Rh(1)—P(1)	2.3008(4)	P(1)—C(20)	1.827(2)
C(28)—O(1)	1.132(3)	C(20)—C(21)	1.417(3)
P(1)—C(19)	1.831(2)	C(20)—C(25)	1.412(3)
C(11) —C(12)	1.501(3)	C(12) —C(17)	1.399(3)
Bond Angles (º)			
O(1)-C(28)-Rh(1)	177.5(2)	P(1)-Rh(1)-C(11)	82.15(6)
C(28)-Rh(1)-C(11)	88.80(9)	Rh(1)-C(11)-C(12)	117.2(1)
C(28)-Rh(1)-P(1)	89.56(7)	Rh(1)-P(1)-C(17)	105.52(6)

8.8. X-Ray structure analysis of 3a·NCCH$_3^+$.

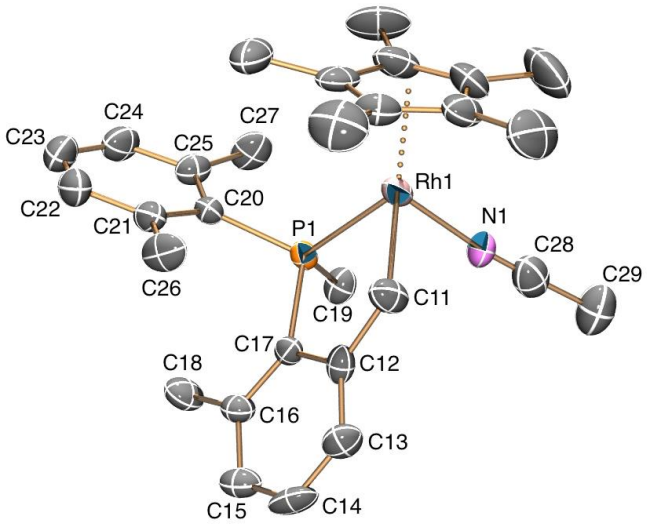


Figure S11. X–ray molecular structure of **3a·NCCH$_3^+$**, with H atoms and BAr_F^- omitted for clarity.

Table S15. Crystal data and structure refinement for **3a·NCCH$_3^+$**.

Empirical formula	$C_{30.5}H_{25}B_{0.5}F_{12}N_{0.5}P_{0.5}Rh_{0.5}$
Formula weight	698.86
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 12.4197(3) Å α = 90º b = 13.0994(2) Å β = 108.6820(10)º c = 19.3734(4) Å γ = 90º
Volume	2985.80(11) Å^3
Z	4
Density (calculated)	1.555 Mg/mm^{-3}
Absorption coefficient	0.428 mm^{-1}
F(000)	1408.0
Crystal size	0.42 × 0.31 × 0.20 mm^3
Theta range for data collection	5.42 to 52.74°
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-24 \le l \le 23$
Reflections collected	45721
Independent reflections	12217 [R(int) = 0.0380]
Completeness to theta = 25.25°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.853 and 0.918
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12217/1/812
Goodness-of-fit on F^2	1.047
Final R indexes [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1426
Final R indexes [all data]	R1 = 0.0594, wR2 = 0.1466
Largest diff. Peak and hole	3.34 and -0.80 e$^-$ Å^{-3}

Table S16. Selected bond lengths [Å] and angles [°] for **3·NCCH$_3^+$**.

Bond Distances			
Rh(1) —N(1)	2.024(4)	C(12)—C(17)	1.401(6)
Rh(1)—C(11)	2.102(5)	P(1)—C(17)	1.813(4)
Rh(1)—P(1)	2.284(1)	P(1)—C(20)	1.852(4)
C(28)—N(1)	1.128(8)	P(1)—C(19)	1.835(6)
C(29)—C(28)	1.49(1)	C(20)—C(25)	1.411(6)
C(11)—C(12)	1.509(8)	C(20)—C(21)	1.412(7)

Bond Angles (º)			
C(29)-C(28)-N(1)	178.3(7)	C(11)-Rh(1)-P(1)	82.0(2)
Rh(1)-N(1)-C(28)	174.8(5)	Rh(1)-C(11)-C(12)	117.7(4)
Rh(1)-P(1)-C(17)	106.7(1)	P(1)-Rh(1)-N(1)	89.7(1)
N(1)-Rh(1)-C(11)	86.2(2)	C(11)-C(12)-C(17)	120.6(5)

8.9. X-Ray structure analysis of $3a{\cdot}C_2H_4^+$.

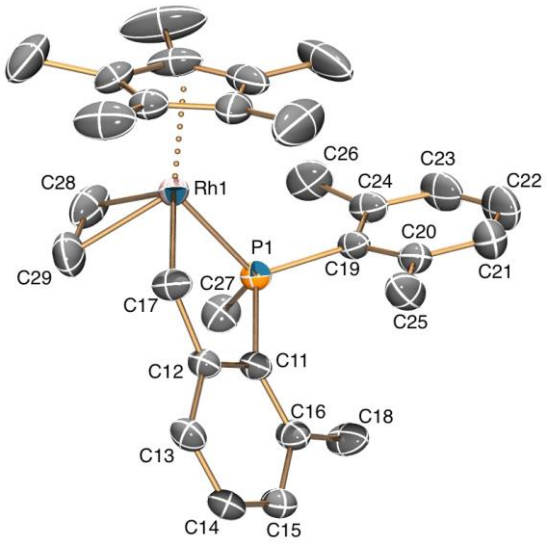


Figure S12. X–ray molecular structure of $3a{\cdot}C_2H_4^+$, with H atoms and BAr_F^- omitted for clarity.

Table S17. Crystal data and structure refinement for $3a{\cdot}C_2H_4^+$.

Empirical formula	$C_{61}H_{51}BF_{24}PRh$
Formula weight	1384.71
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.3850(7) Å α = 87.7530(10)º b = 13.0659(7) Å β = 73.6350(10)º c = 19.5686(11) Å γ = 85.7550(10)º
Volume	3029.4(3) $Å^3$
Z	2
Density (calculated)	1.518 Mg/mm^{-3}
Absorption coefficient	0.421 mm^{-1}
F(000)	1396.0
Crystal size	0.43 × 0.31 × 0.26 mm^3
Theta range for data collection	2.16 to 61.02°
Index ranges	$-17 \le h \le 17$, $-18 \le k \le 18$, $-27 \le l \le 27$
Reflections collected	103522
Independent reflections	18249 [R(int) = 0.0273]
Completeness to theta = 25.25°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8984 and 0.8397
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	18249/0/895
Goodness-of-fit on F^2	1.033
Final R indexes [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.1058
Final R indexes [all data]	R1 = 0.0513, wR2 = 0.1151
Largest diff. Peak and hole	1.15 and -0.75 e^- $Å^{-3}$

Table S18. Selected bond lengths [Å] and angles [°] for **3a·$C_2H_4^+$**.

Bond Distances			
Rh(1) —C(29)	2.190(3)	C(12)—C(11)	1.401(3)
Rh(1)—C(28)	2.217(2)	C(11)—P(1)	1.819(2)
Rh(1)—C(17)	2.132(2)	P(1)—C(19)	1.833(2)
Rh(1)—P(1)	2.3020(5)	P(1)—C(27)	1.835(2)
C(29)—C(28)	1.369(4)	C(12)—C(13)	1.398(3)
C(19)—C(20)	1.407(3)	C(19)—C(24)	1.422(3)
C(17)—C(12)	1.499(3)	C(11)—C(16)	1.408(3)

Bond Angles (º)			
Rh(1)-C(28)-C(29)	70.9(2)	P(1)-Rh(1)-C(29)	94.24(7)
C(28)-C(29)-Rh(1)	73.0(2)	C(28)-Rh(1)-C(17)	113.75(9)
C(28)-Rh(1)-C(29)	36.2(1)	C(29)-Rh(1)-C(17)	78.80(9)
C(12)-C(17)-Rh(1)	118.0(1)	C(11)-P(1)-Rh(1)	106.33(6)
C(28)-Rh(1)-P(1)	90.60(7)	P(1)-Rh(1)-C(17)	80.84(6)

9. Theoretical Calculations

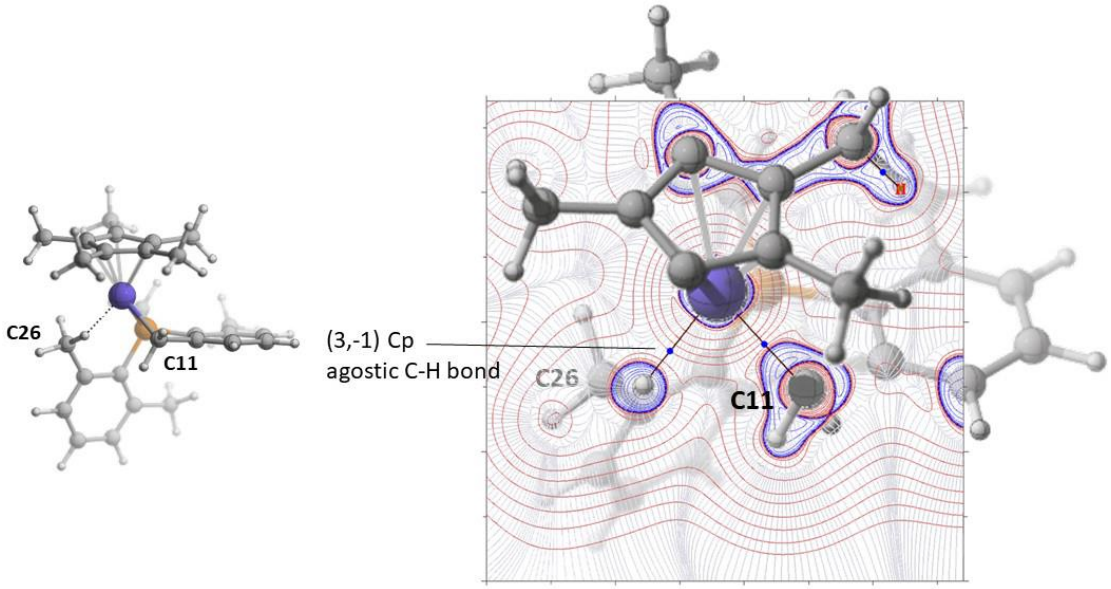


Figure S13. A representation of the Laplacian of the electron density ($\nabla^2\boldsymbol{\rho}$) of $\mathbf{A}^+$ on the H(C26)-Rh1-C11 plane. The blue contour lines correspond to negative values of the Laplacian (charge accumulation regions) and the red contour lines correspond to positive values (charge depletion regions). Two blue dots and black lines represent bond critical points (*bcp*) of the electron density ($\boldsymbol{\rho}$) and bond paths connecting the Rh1 atom and the C11 and H(C26) atoms.

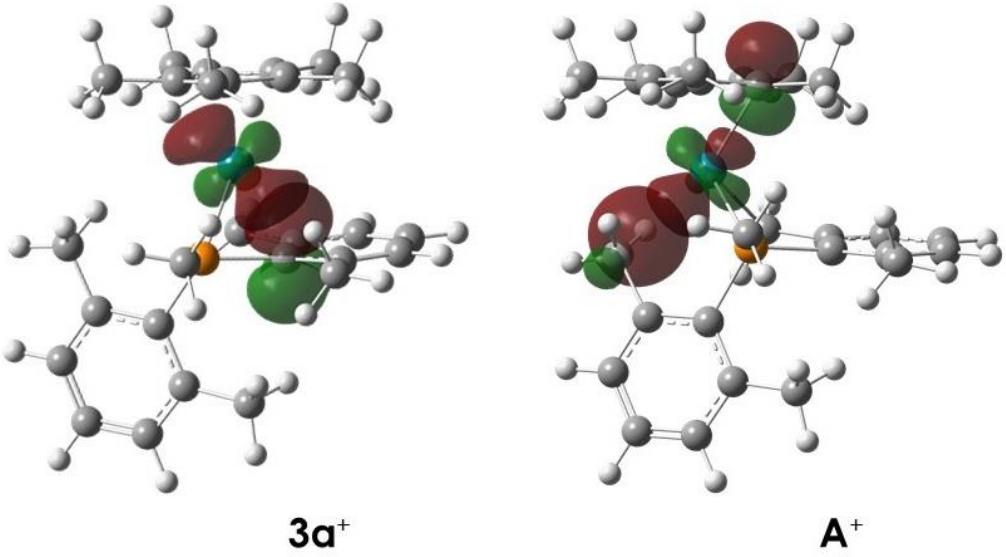


Figure S14. Donor-acceptor interactions in $\mathbf{3a}^+$ and $\mathbf{A}^+$ according to second order perturbation theory analysis of Fock matrix in NBO basis. The figure to the left shows the filled π NBO that connects the atoms C17 and C12 of the cyclometalated xylyl ring of $\mathbf{3a}^+$, which is delocalized onto one empty NBO localized on the rhodium atom. The figure to the right represents a filled C—H σ NBO of one of the methyl fragments of the non-metalated xylyl ring of $\mathbf{A}^+$, which is delocalized onto an antibonding (empty) σ* NBO that connects the rhodium atom and the Cp ring.

Table S19. Selected Wiberg bond indices for **3a**$^+$ and **A**$^+$. Note a decrease in the bond indices between Rh1 and C12 and C17 and an increase in the bond indices between Rh1 and C26 and H(C26) from **3a**$^+$ and **A**$^+$.

Bond	WBI	
	3a$^+$	**A**$^+$
R1-P1	0.4174	0.4618
Rh1-C17	0.2072	0.0177
Rh1-C12	0.1556	0.0128
Rh1-C11	0.4375	0.5221
Rh1-H(C26)	0.0027	0.0554
Rh1-C26	0.0042	0.0808

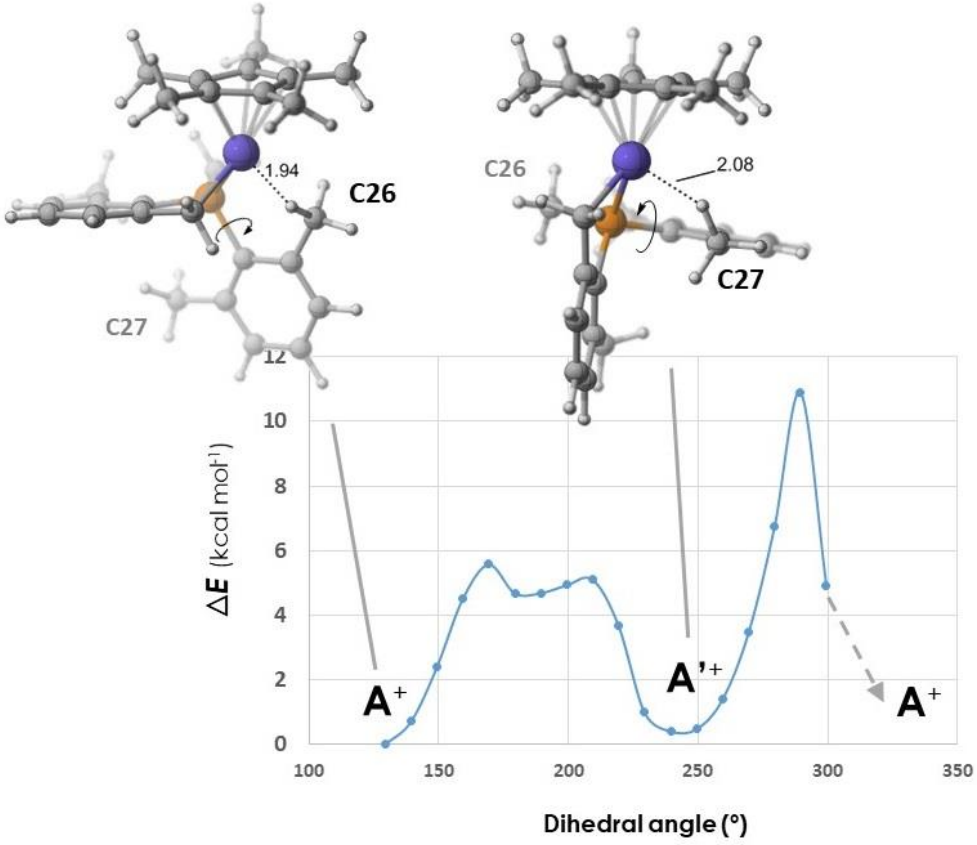
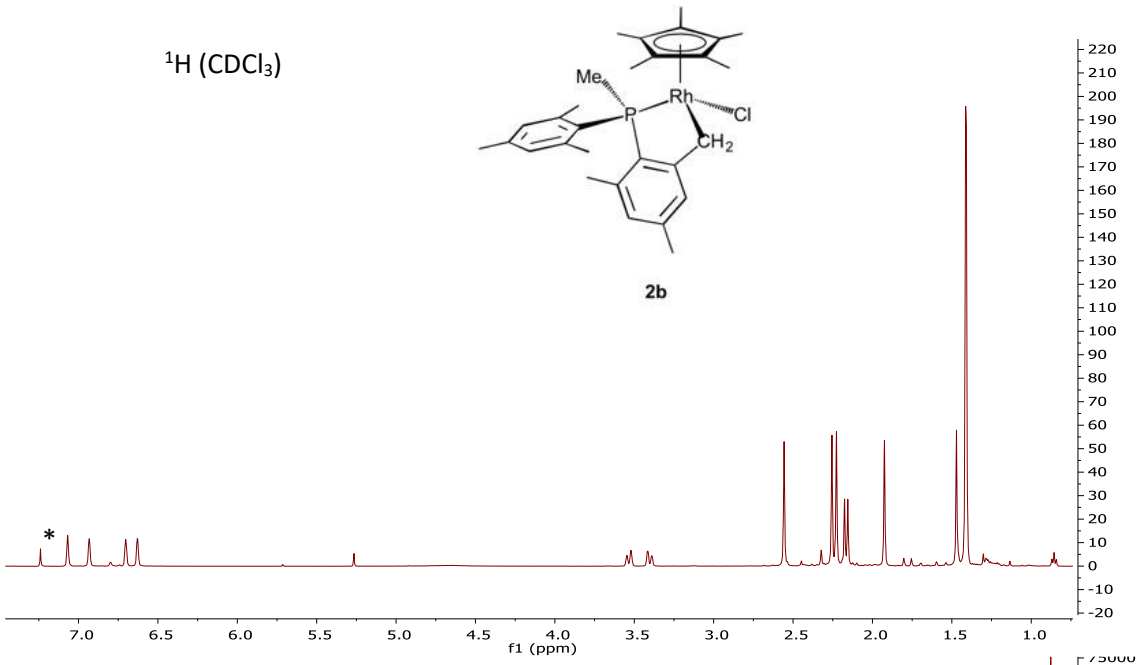


Figure S15. Relaxed Potential Energy (PES) scan for the rotation of the non-metalated xylyl ring of **A**$^+$. The overall energy barrier is *ca*. 10 kcal·mol^{-1} from **A**$^+$, or *ca*. 15 kcal·mol^{-1} from **3a**$^+$. Note the three local maxima along the C21-C20-P1-C17 dihedral angle and an intermediate local minimum, **A'**$^+$, which features a slightly different conformation of the κ*C*, κ*P* coordinated ligand. Both minima, **A**$^+$ and **A'**$^+$, have very similar stability and are in fast equilibrium. For this reason, they have been discussed as a single intermediate in the main text. To be precise, **A**$^+$ is connected to **3a**$^+$ through the first TS of Figure C1, and it is **A'**$^+$ which evolves through the second TS to the Rh(V) intermediate **B**$^+$.

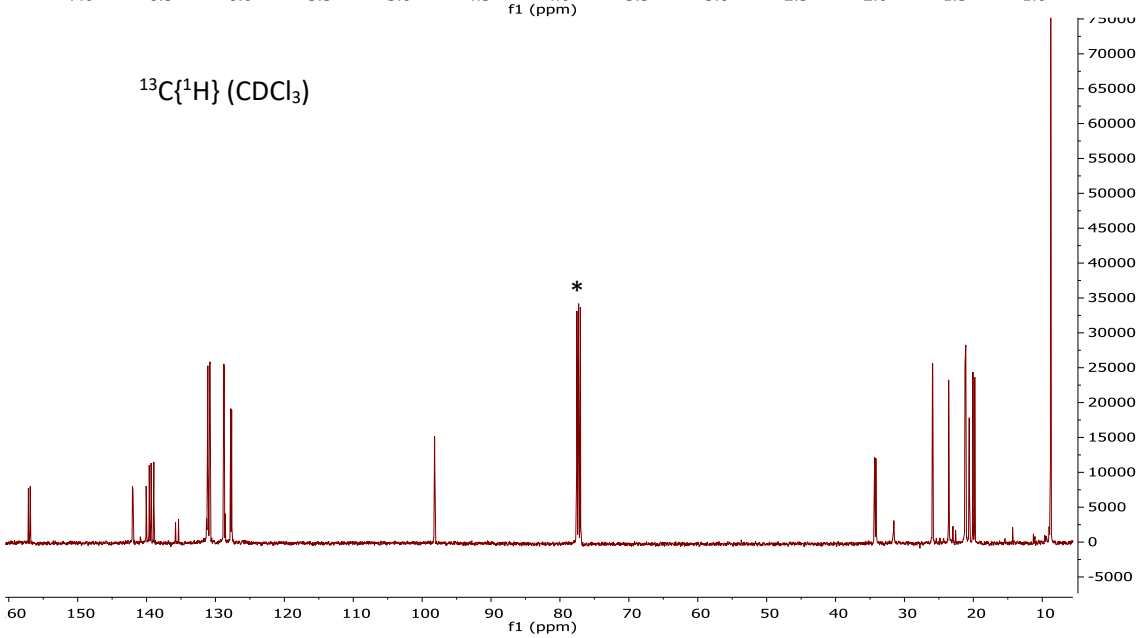
11. NMR spectra of new compounds

2b

^{1}H ($CDCl_3$)

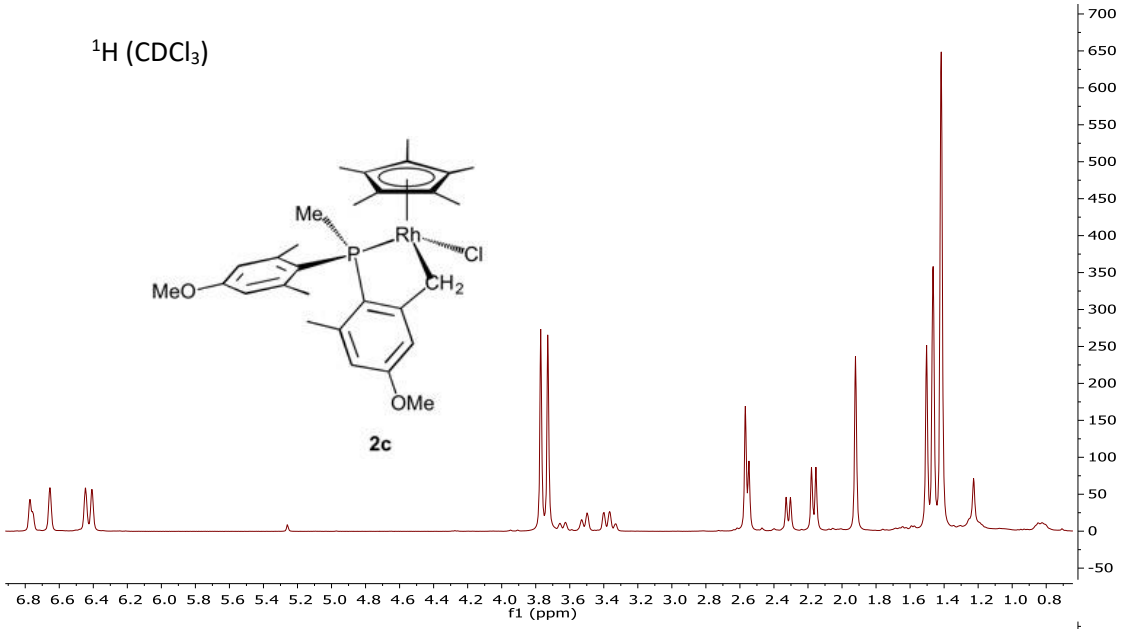


$^{13}C\{^{1}H\}$ ($CDCl_3$)

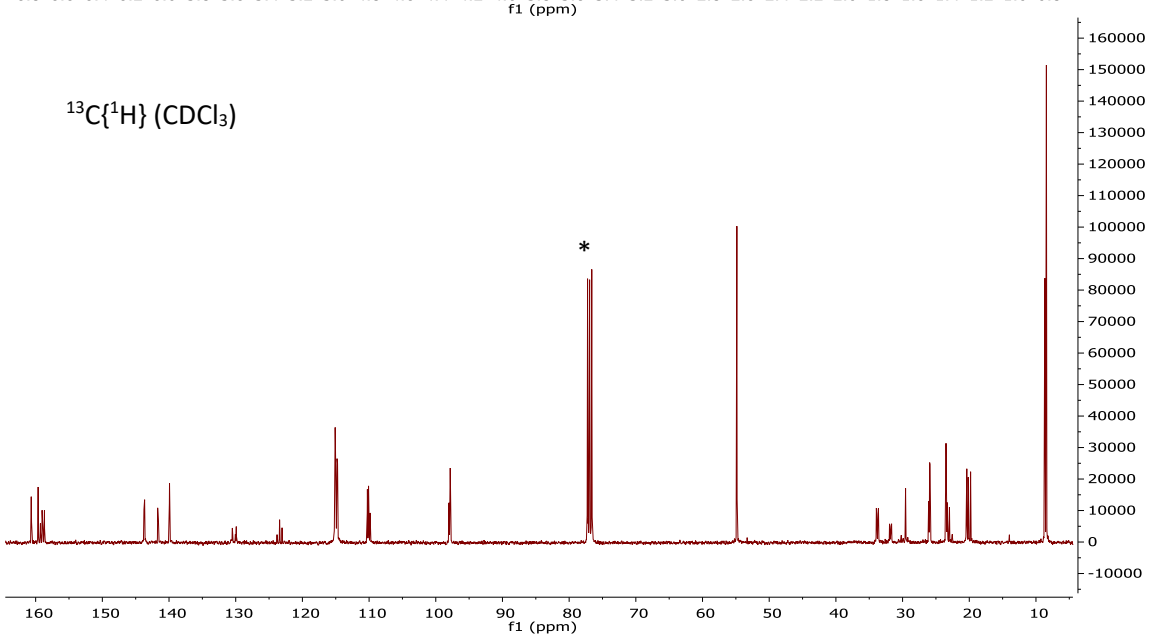


2c

^{1}H ($CDCl_3$)

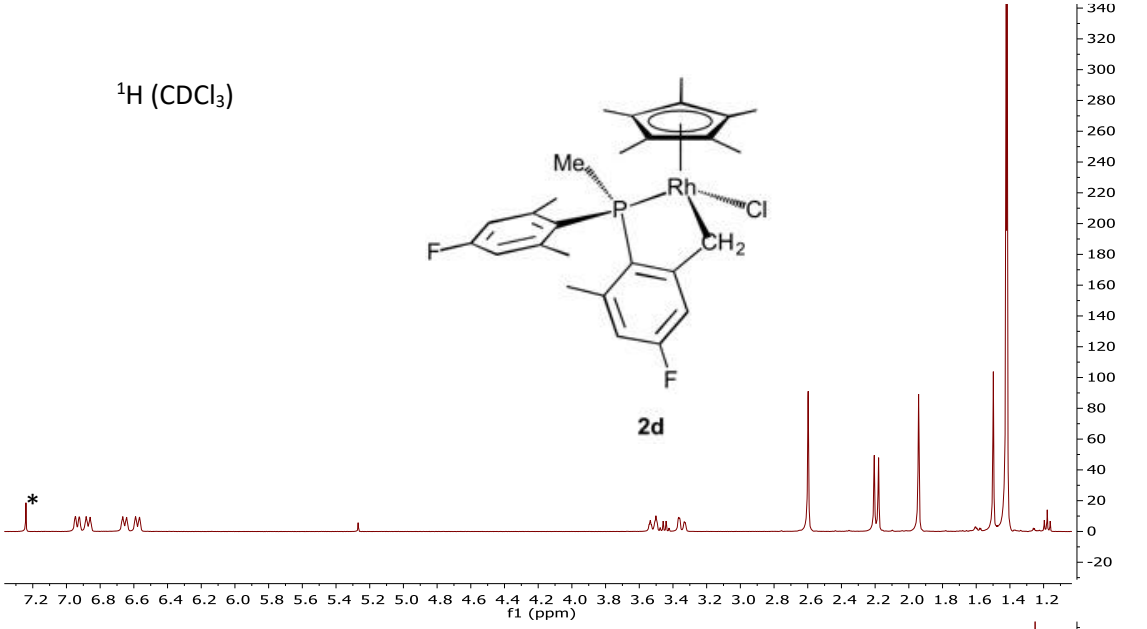


$^{13}C\{^{1}H\}$ ($CDCl_3$)

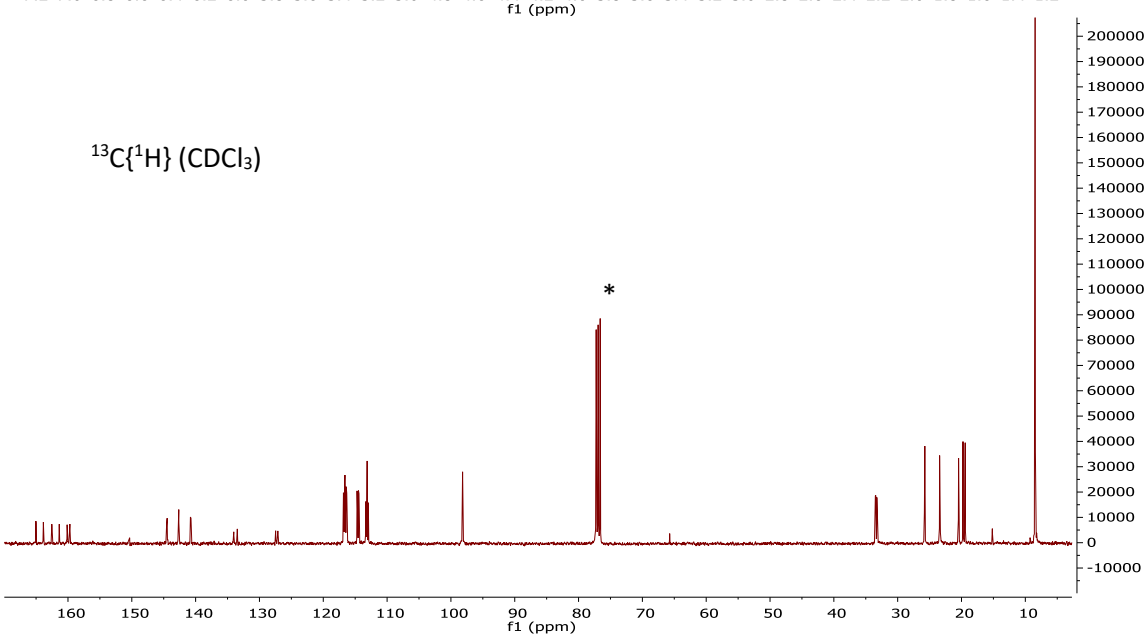


2d

^{1}H ($CDCl_3$)

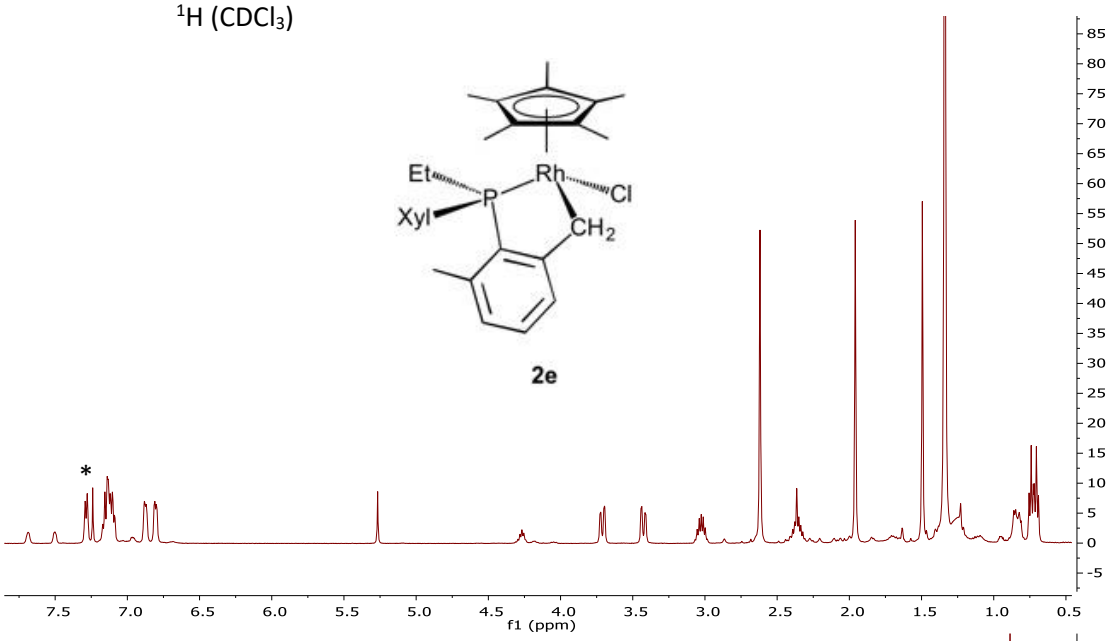


$^{13}C\{^{1}H\}$ ($CDCl_3$)

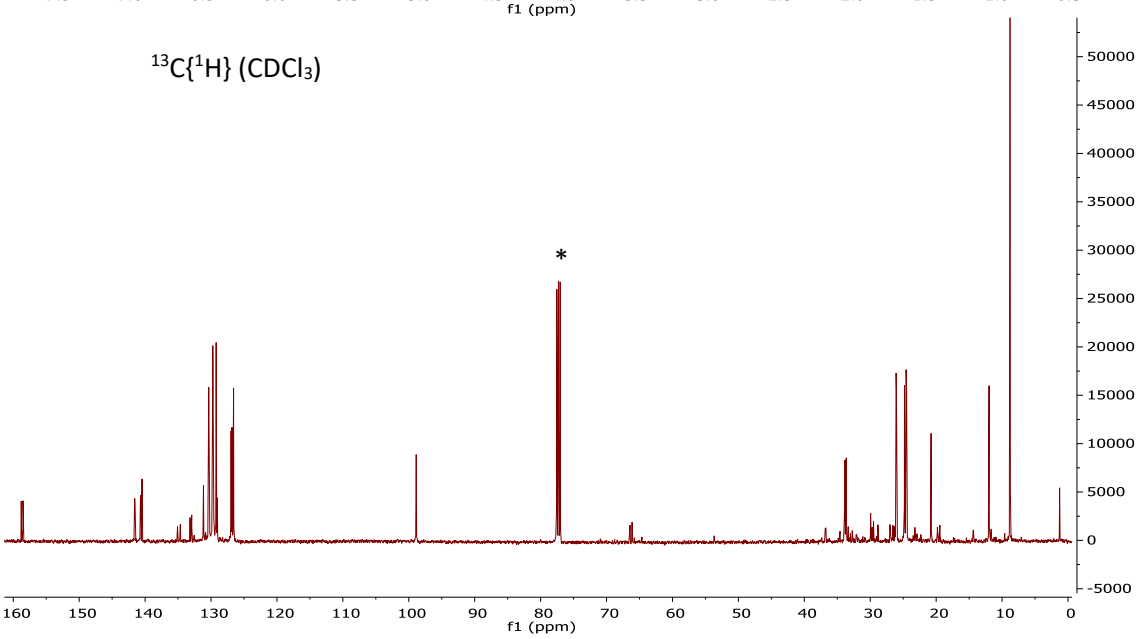


2e

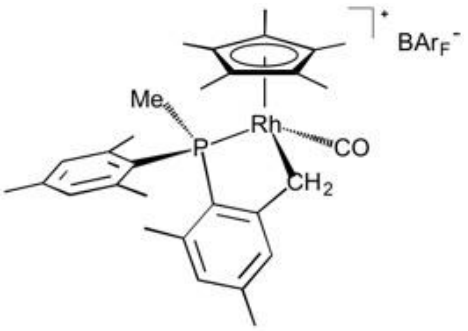
^{1}H ($CDCl_3$)



$^{13}C\{^{1}H\}$ ($CDCl_3$)



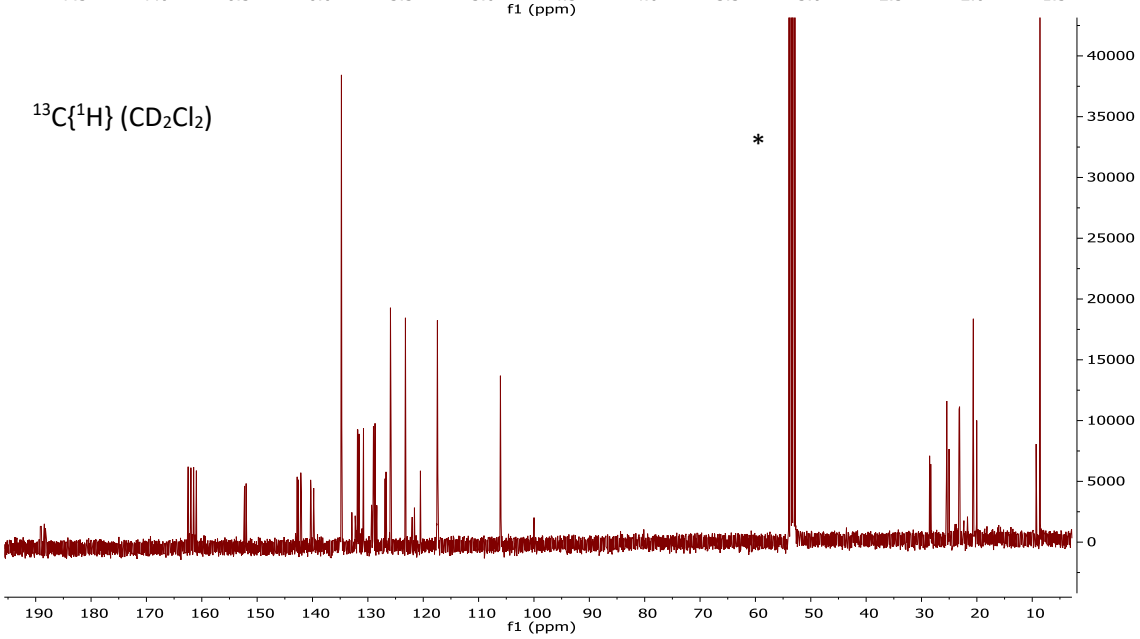
3b·CO⁺



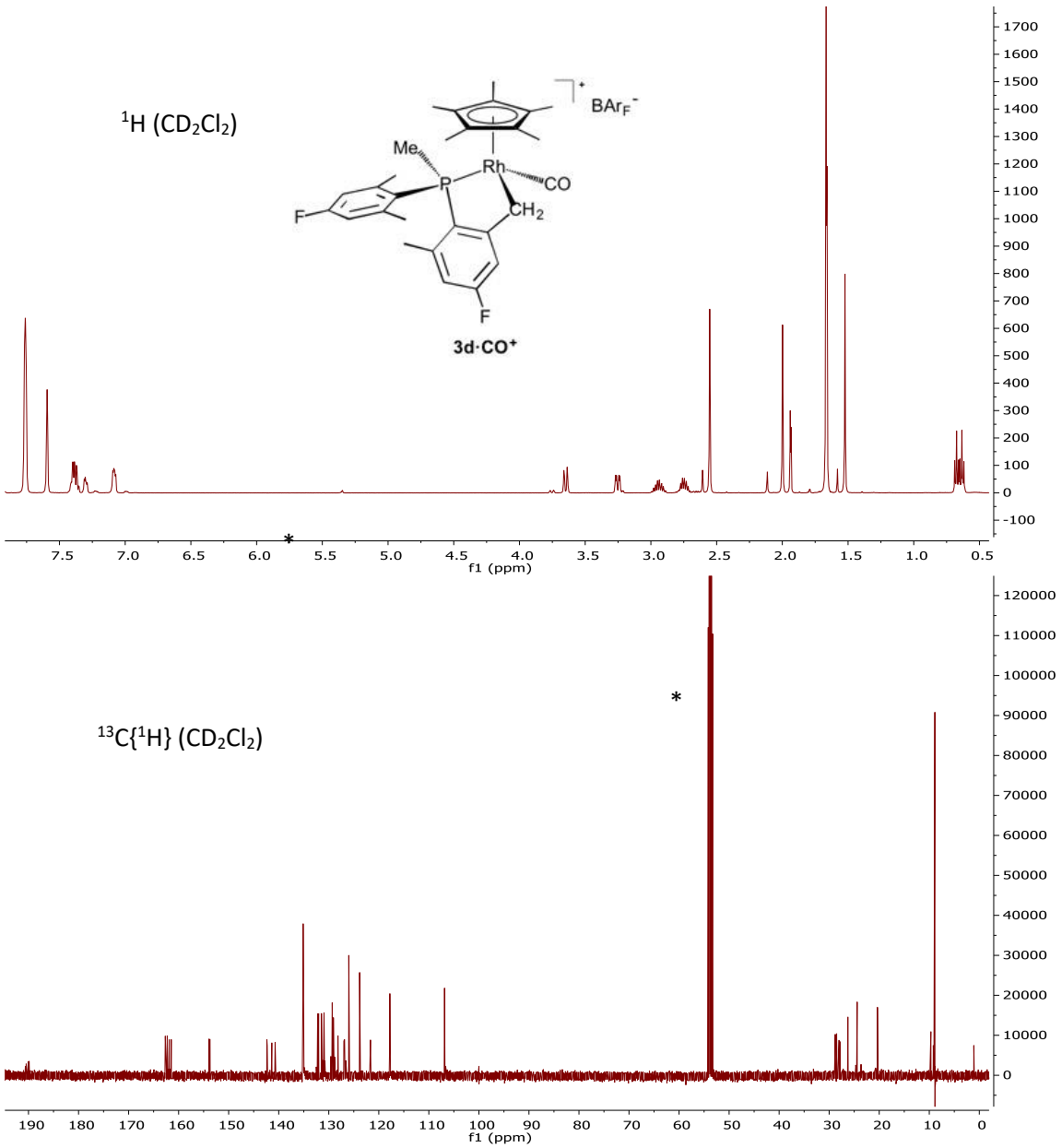
3b·CO⁺

^{1}H (CD_2Cl_2)

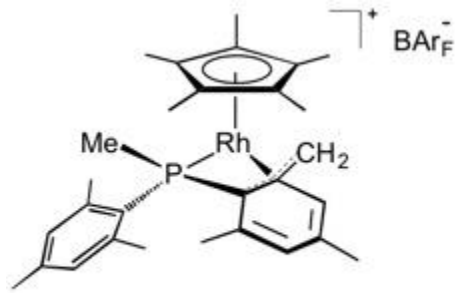
$^{13}C\{^1H\}$ (CD_2Cl_2)



3d·CO⁺



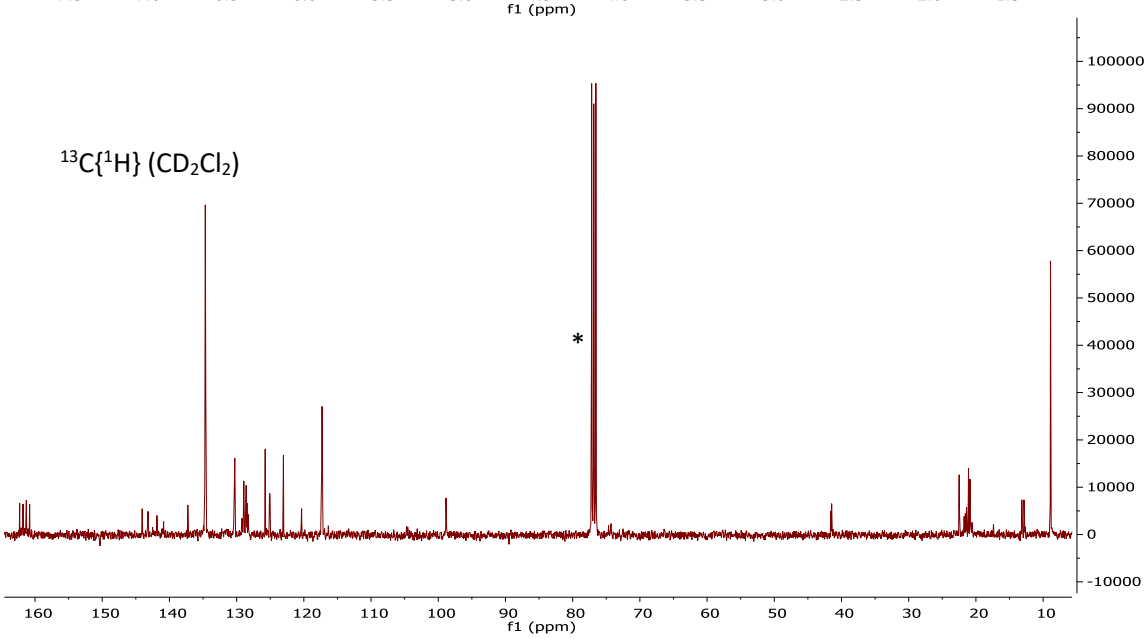
3b⁺

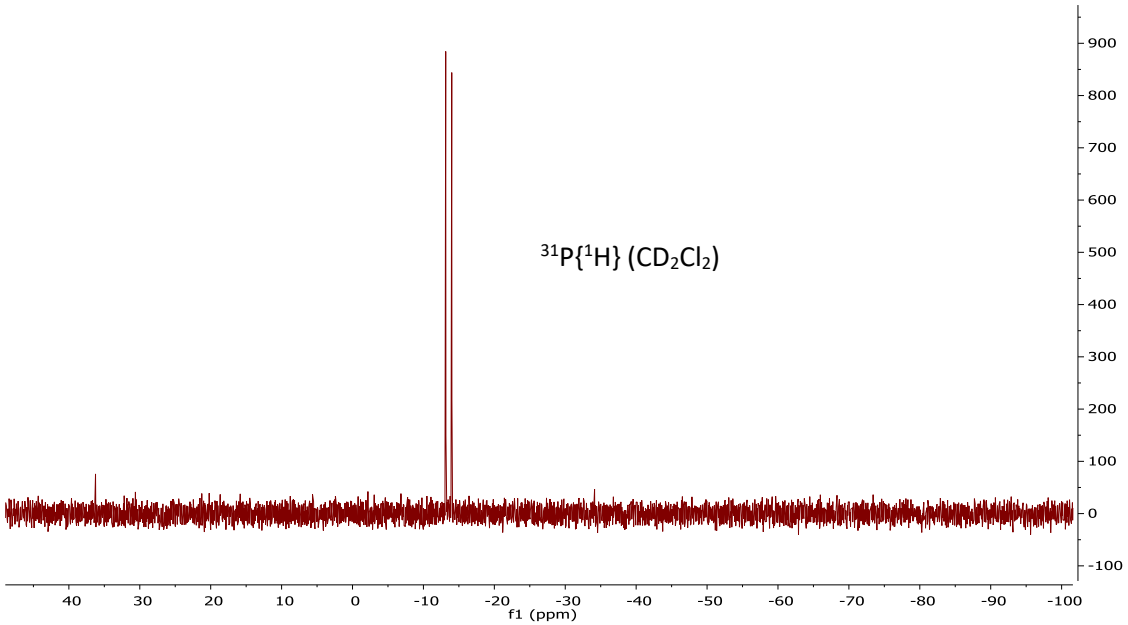


3b⁺

^{1}H (CD_2Cl_2)

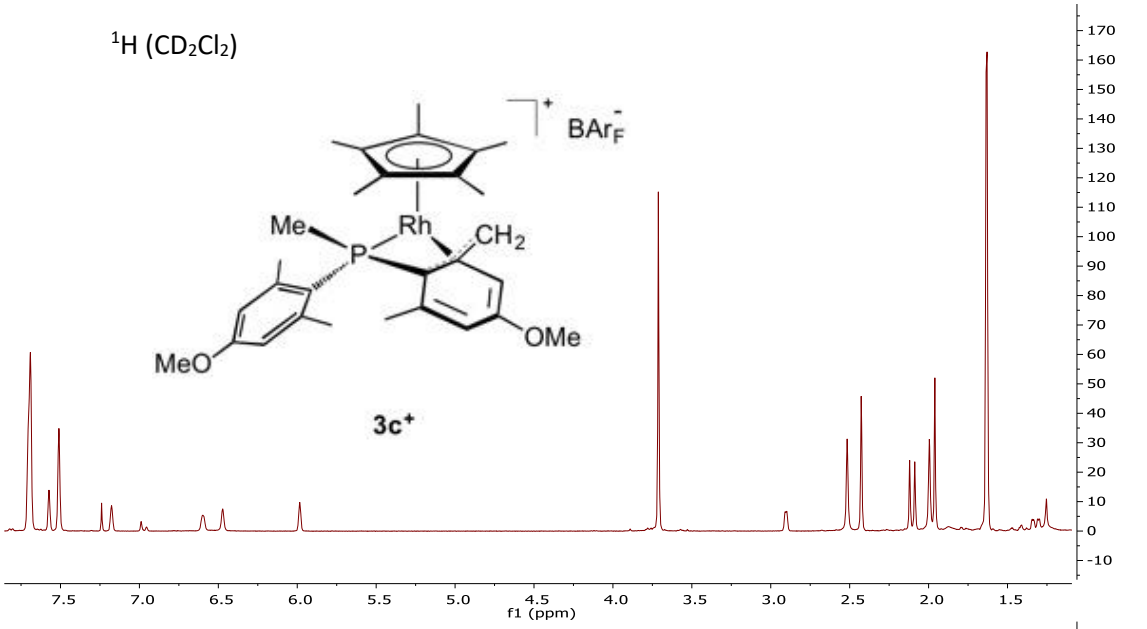
$^{13}C\{^1H\}$ (CD_2Cl_2)



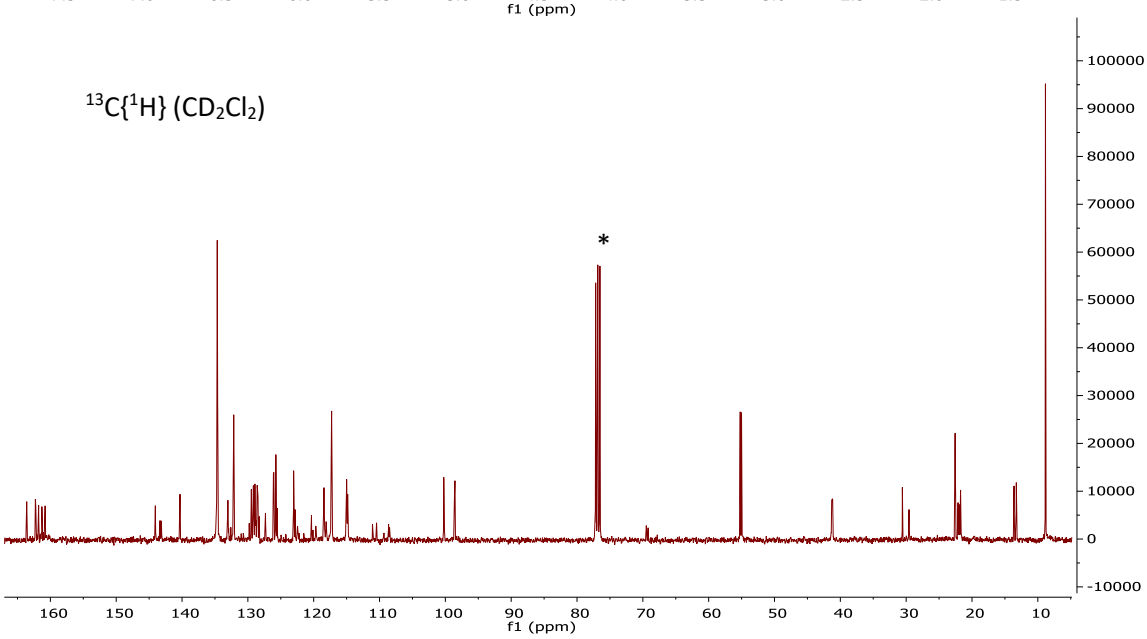

$^{31}P\{^{1}H\}$ (CD_2Cl_2)
900
800
700
600
500
400
300
200
100
0
-100
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

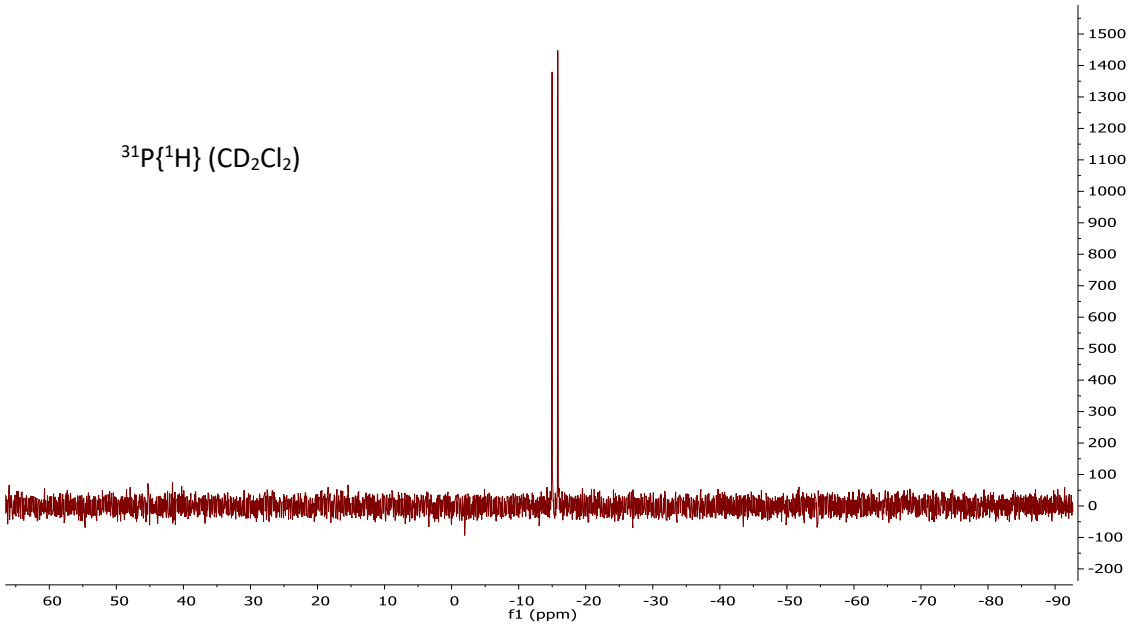
3c$^+$

^{1}H (CD_2Cl_2)



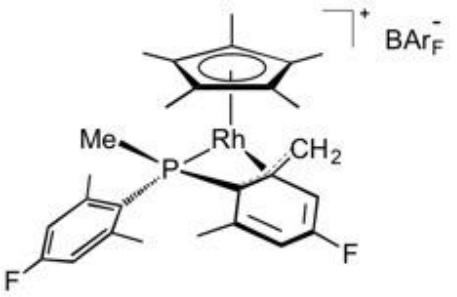
^{13}C{^{1}H} (CD_2Cl_2)




$^{31}P\{^{1}H\}$ (CD_2Cl_2)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

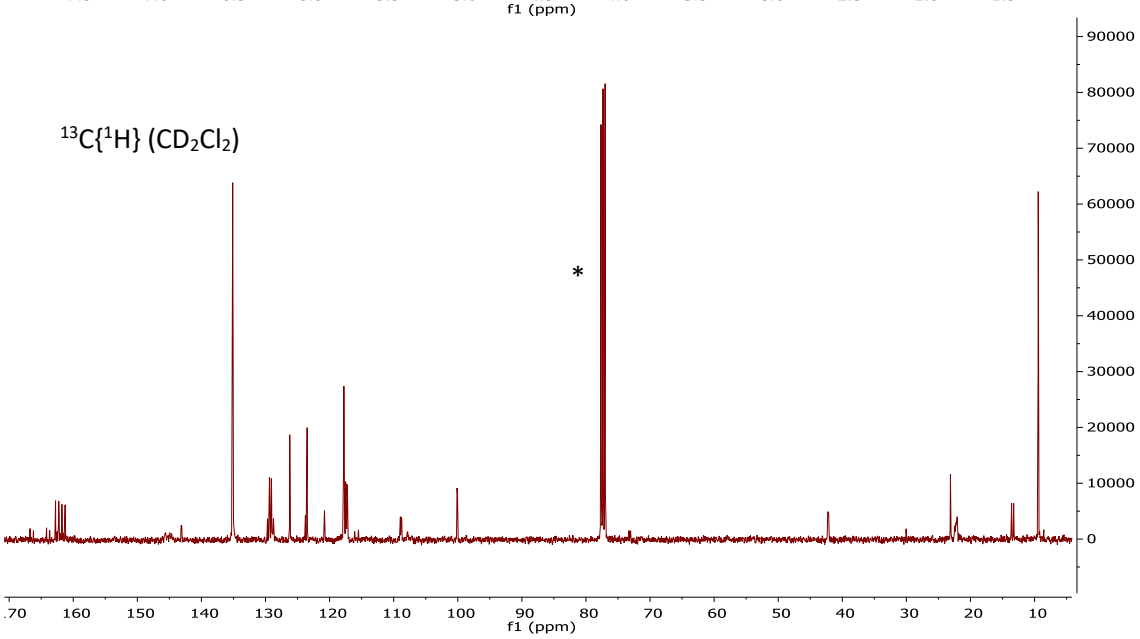
3d⁺

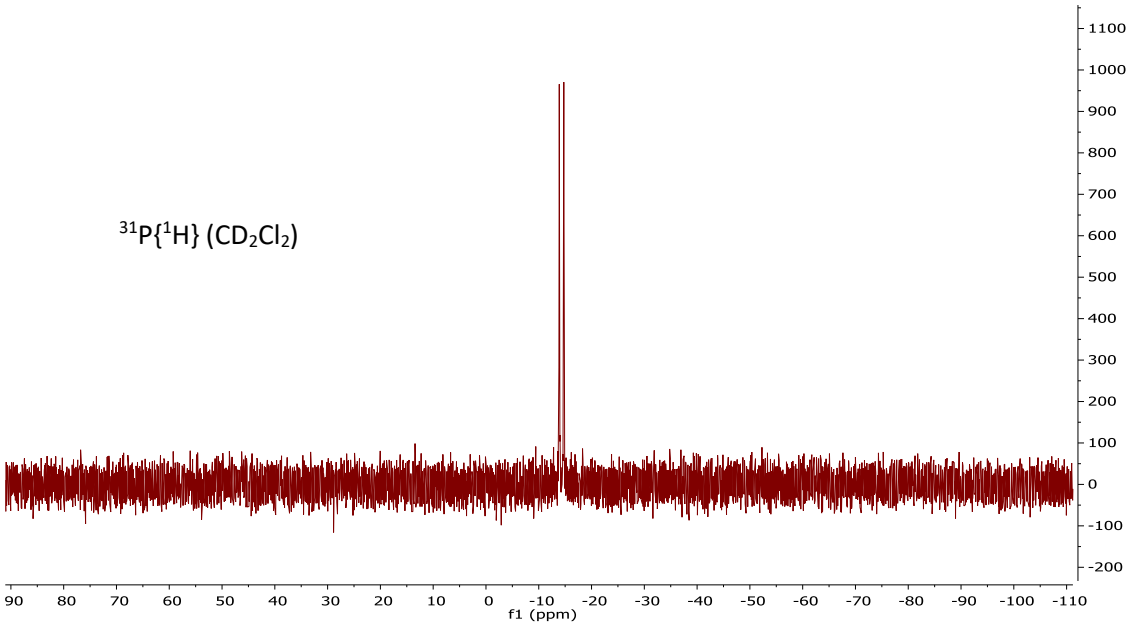
^{1}H (CD_2Cl_2)



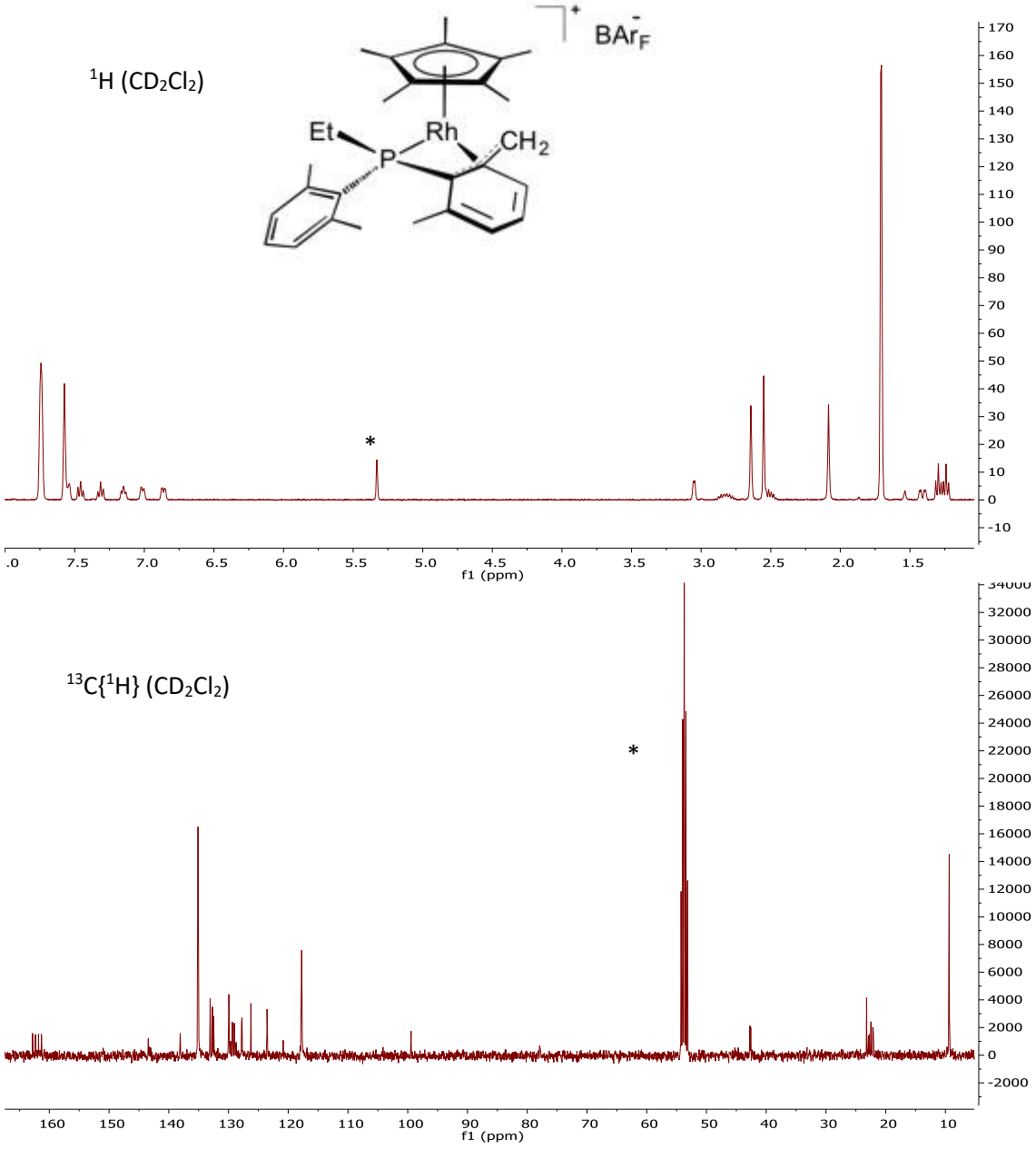
3d⁺

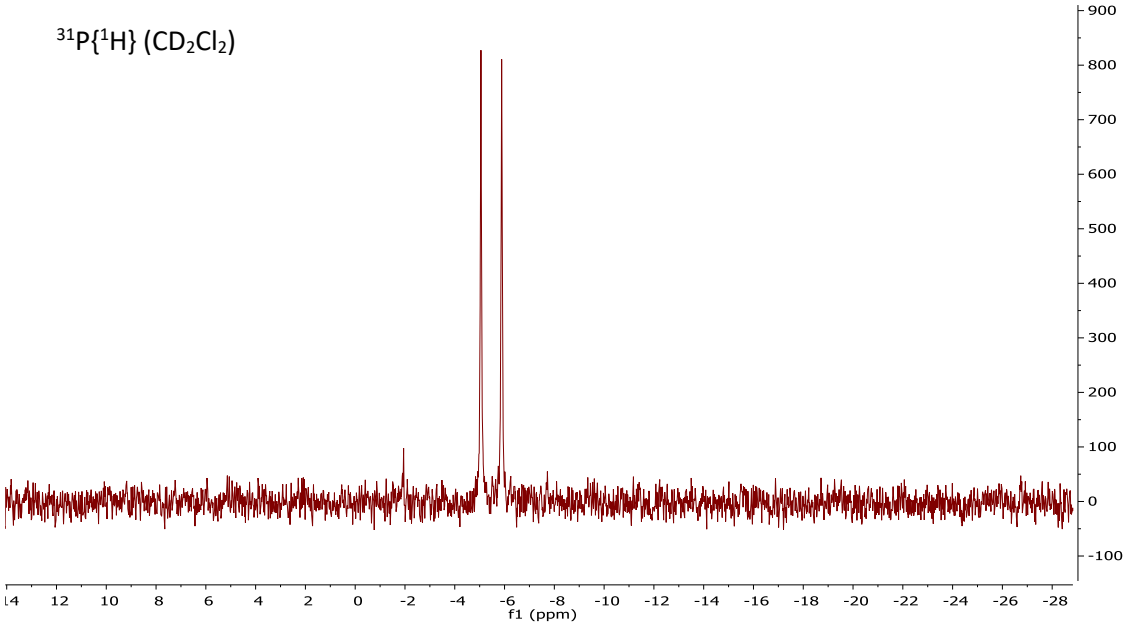
$^{13}C\{^{1}H\}$ (CD_2Cl_2)




$^{31}P\{^{1}H\}$ (CD_2Cl_2)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

3e^{+}





12. References.

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