Supplementary Information

Synthesis and Structure of Rhodium(I) Silyl Carbonyl Complexes: Photochemical C–F and C–H Bond Activation of Fluorinated Aromatic Compounds

Lada Zámostná [a], Stefan Sander [a], Thomas Braun [a,*], Reik Laubenstein [a], Beatrice Braun [a], Roy Herrmann [a] and Paul Kläring [a]

[a]Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Straße 2,

D-12489 Berlin, Germany. E-mail: thomas.braun@chemie.hu-berlin.de

Computational details

All calculations were run using the B3LYP functional as implemented in the Gaussian 09 (Revision A.02) program package.[1,2] For the carbon and hydrogen atoms of the isopropyl groups 6-31g* basis sets was employed.[3] Rhodium atoms were described using RECPs with the associated cc-pVDZ-PP basis set.[4] Cc-pVTZ basis sets were employed for all other atoms.[5] All structure optimizations were performed in C_1 symmetry without any geometrical constraints. Frequency mode analyses were run for all stationary points to identify them as minima (no negative eigenvalues). Molecular orbitals have been visualized with the GaussView 3.0 program. Cartesian coordinates for the optimized structures are given below.

Figures S1 and S2 show the DFT/B3LYP optimized structures for [Rh{Si(OEt)$_3$}(CO)(dippp)] (**1**) and [Rh{Si(OEt)$_3$}-(CO)(dippe)] (**2**). Selected calculated bond lengths and angles of **1** and **2** are given in tables T1 and T2, respectively and are in agreement with the geometries obtained from the crystal structure analyses. Selected molecular orbitals of compounds **1** and **2** are depicted in figure S3.

Molecular orbitals were also calculated for the geometries obtained from the crystal structures of [{Rh(μ-CO)(dippp)}$_2$] (**10**) and [{Rh(μ-CO)(dippe)}$_2$] (**11**). Figure S4 shows selected molecular orbitals of **10** and **11**. In both cases the shape of a energetically low molecular orbital (HOMO−8) indicates a Rh–Rh σ-interaction.

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2 G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, X. L. M. Caricato, H. P. Hratchian, A. F. Izmaylov, G. Z. J. Bloino, M. H. J. L. Sonnenberg, K. T. M. Ehara, J. H. R. Fukuda, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *in Gaussian 09, Revision A.02, Gaussian Inc., Wallingford CT*, **2009**.

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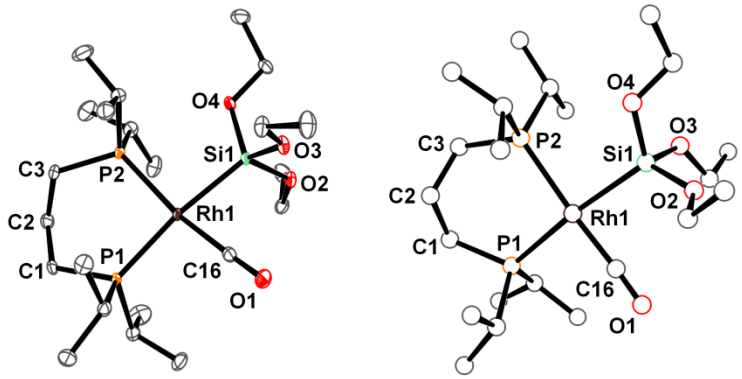


Figure S1. Molecular Structure of **1** (left: crystal structure, right: DFT optimized structure); hydrogen atoms have been omitted for clarity.

Table T1 Selected calculated bond lengths (Å) and angles (°) for **1** (experimental values are given in square brackets).

Bond	Length	Bond	Angle
Rh1–P1	2.409 [2.3524(5)]	P1–Rh1–P2	94.6 [94.243(18)]
Rh1–P2	2.406 [2.3608(5)]	P2–Rh1–Si1	90.3 [92.490(18)]
Rh1–Si1	2.406 [2.3581(5)]	Si1–Rh1–C16	83.6 [79.70(6)]
Rh1–C16	1.846 [1.840(2)]	P1–Rh1–C16	92.5 [94.10(6)]
C16–O1	1.153 [1.148(2)]	P1–Rh1–Si1	170.2 [172.494(19)]
		P2–Rh1–C16	170.2 [168.55(6)]
		Rh1–C16–O1	176.5 [176.96(19)]

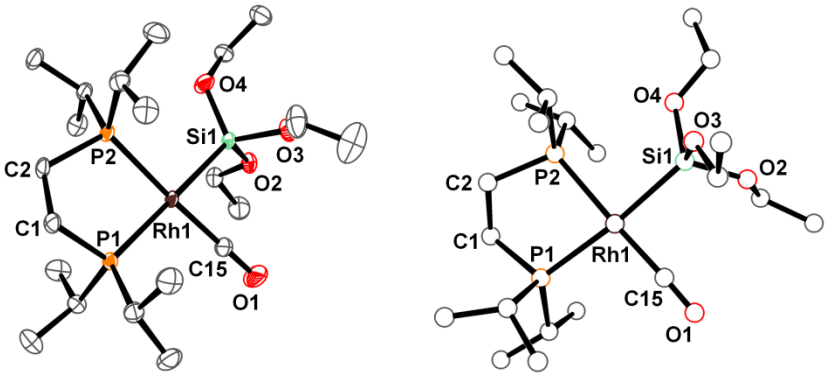
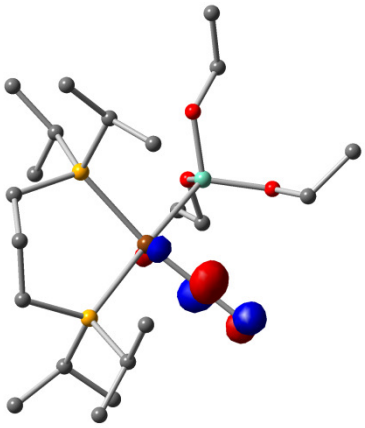


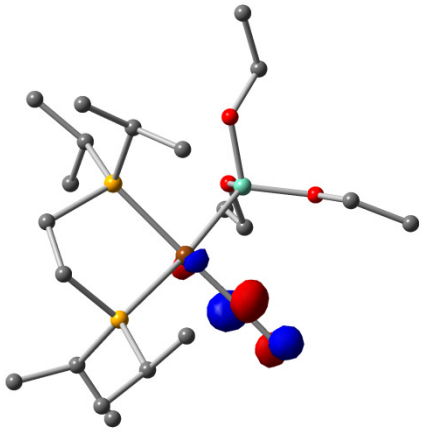
Figure S2. Molecular Structure of **2** (left: crystal structure, right: DFT optimized structure); hydrogen atoms have been omitted for clarity.

Table T2 Selected calculated bond lengths (Å) and angles (°) for **2** (experimental values are given in square brackets).

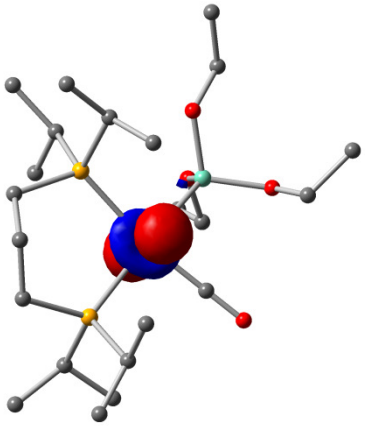
Bond	Length	Bond	Angle
Rh1–P1	2.377 [2.3386(4)]	P1–Rh1–P2	84.4 [85.107(14)]
Rh1–P2	2.384 [2.3475(4)]	P2–Rh1–Si1	90.6 [94.859(15)]
Rh1–Si1	2.395 [2.3552(4)]	Si1–Rh1–C15	87.1 [82.53(5)]
Rh1–C15	1.856 [1.8455(16)]	P1–Rh1–C15	97.8 [97.53(5)]
C15–O1	1.152 [1.146(2)]	P1–Rh1–Si1	173.6 [178.130(14)]
		P2–Rh1–C15	177.5 [177.18(5)]
		Rh1–C15–O1	178.2 [179.66(18)]



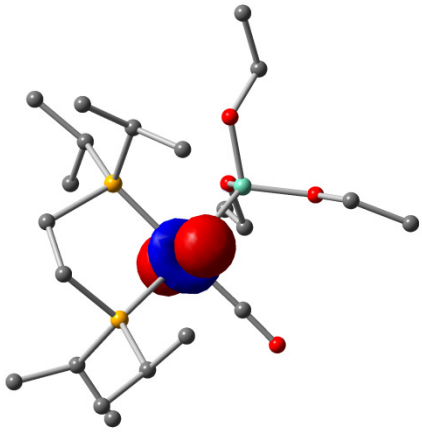
LUMO (138) / E = –0.035 eV = –0.95 eV



LUMO (134) / E = –0.036 eV = –0.980 eV

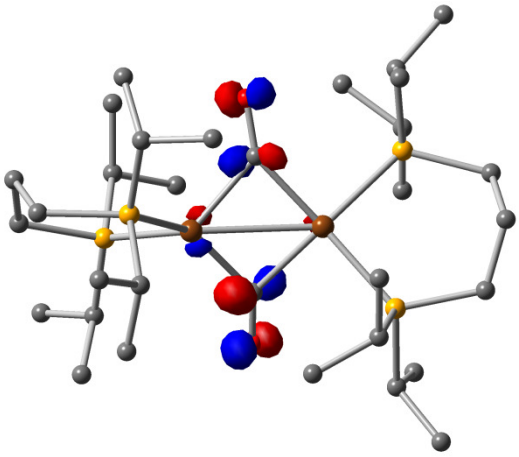


HOMO (137) / E = –0.181 H = –4.93 eV

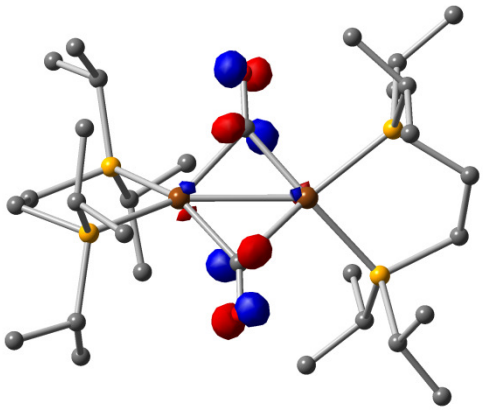


HOMO (133) / E = –0.181 eV = –4.93 eV

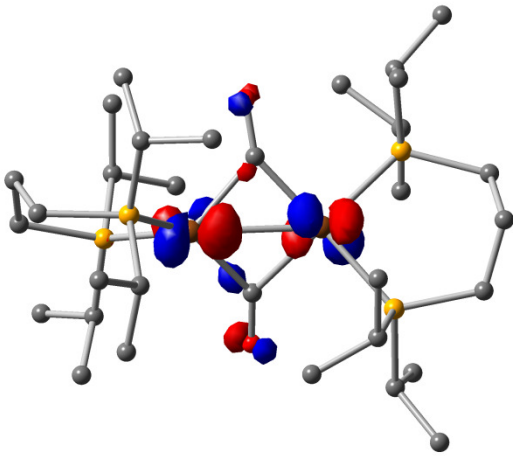
Figure S3. Selected molecular orbitals of **1** (left) and **2** (right) and their energies; hydrogen atoms have been omitted for clarity; ε = 0.08.



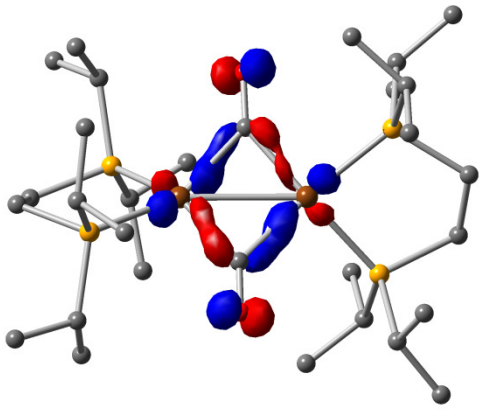
LUMO (186) / E = –0.021 eV



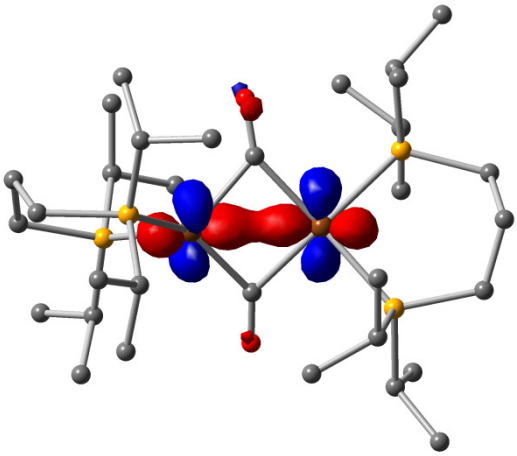
LUMO (178) / E = –0.028 eV



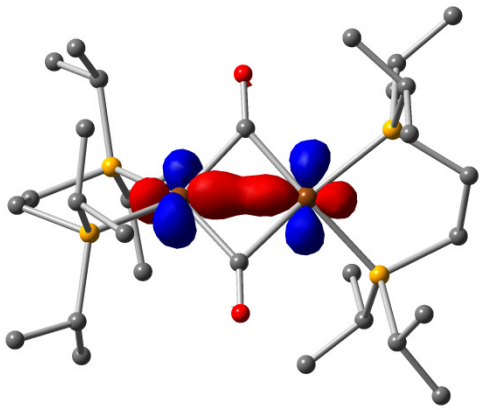
HOMO (185) / E = –0.140 eV



HOMO (177) / E = –0.138 eV



HOMO–8 (177) / E = –0.236 eV



HOMO–8 (169) / E = –0.236 eV

Figure S4. Selected molecular orbitals of **10** (left) and **11** (right) and their energies; hydrogen atoms have been omitted for clarity; ε = 0.08.

Optimized cartesian coordinates for compound **1**:

79

Rh	-1.69599	0.69631	0.99466
Si	0.05955	2.30786	0.66274
O	0.11574	-0.39298	3.12053
O	1.11436	1.85777	-0.56266
O	1.12820	2.59241	1.92892
O	-0.44943	3.82596	0.13191
P	-3.18349	-1.18997	1.17400
P	-3.13484	1.93917	-0.48015
C	-0.55056	0.01726	2.27330
C	-4.86834	-1.08377	0.37522
C	-4.72874	1.10304	-0.96084
C	-5.42971	0.32847	0.16509
C	2.06219	0.80853	-0.46598
C	0.79818	2.91625	3.26745
C	0.46559	4.84497	-0.26764
C	-0.26628	6.16956	-0.39117
C	2.76186	0.63313	-1.80213
C	1.40978	4.24952	3.66846
H	-5.40214	1.85669	-1.36573
H	-4.50514	0.41974	-1.78264
H	-6.48737	0.22954	-0.09369
H	-5.40111	0.89711	1.09564
H	-4.79179	-1.56541	-0.60038
H	-5.57008	-1.68323	0.95662
H	0.92122	4.57054	-1.22352
H	1.27530	4.92924	0.46253
H	1.56457	-0.12623	-0.18000
H	2.79163	1.03934	0.31643
H	1.17915	2.12382	3.91819
H	-0.28843	2.94825	3.40943
H	-1.06291	6.10721	-1.13443
H	0.42303	6.95877	-0.69832
H	-0.71213	6.45615	0.56238
H	2.04333	0.38235	-2.58367
H	3.50311	-0.16676	-1.74481
H	3.27016	1.55370	-2.09143
H	2.49093	4.22909	3.52653
H	1.20438	4.46391	4.71984
H	1.00239	5.06265	3.06662
C	-3.22022	3.09960	-3.15864
C	-3.68086	3.58970	0.25584
C	-2.44606	-2.72849	0.35471
C	-4.98860	4.18882	-0.28707
C	-3.73908	3.53299	1.79352
C	-4.23522	-0.42706	3.65531
C	-2.36000	2.32641	-2.14726
C	-1.80490	1.03300	-2.76986
C	-1.20670	-3.23691	1.11039
C	-3.39168	-3.89849	0.02456
C	-3.55542	-1.62588	2.96794
C	-4.33629	-2.92053	3.24100
H	-5.10790	5.20697	0.10456
H	-5.02286	4.25168	-1.37766
H	-5.86329	3.61625	0.04466
H	-2.84108	4.23955	-0.01212
H	-3.87419	4.54574	2.19463
H	-2.82161	3.11235	2.21454
H	-4.58381	2.92755	2.14553
H	-0.46851	-2.44764	1.27012
H	-0.72431	-4.03400	0.53138
H	-1.47067	-3.65936	2.08703
H	-4.26622	-3.59385	-0.55754
H	-3.74878	-4.41171	0.92159
H	-2.84632	-4.63754	-0.57614
H	-2.09708	-2.30904	-0.59963
H	-5.30957	-2.93420	2.73605
H	-4.53188	-3.00997	4.31732
H	-3.78333	-3.81239	2.93589
H	-4.29833	-0.60426	4.73604
H	-3.67810	0.50114	3.49259
H	-5.25962	-0.28221	3.28968
H	-2.55504	-1.73116	3.40626
H	-1.21355	1.27688	-3.66090
H	-2.60500	0.35200	-3.08845
H	-1.15360	0.50234	-2.06815
H	-3.48497	4.09898	-2.80189
H	-4.14557	2.56928	-3.41407
H	-2.65523	3.22830	-4.09069
H	-1.50692	2.95158	-1.86539

SCF Energy = −2251.81457621

Optimized cartesian coordinates for compound **2**:

76

Rh	-1.42785	0.74541	1.09823
Si	0.15090	2.48627	0.63850
O	0.59178	-0.42438	2.99523
O	1.23662	2.14469	-0.59498
O	1.19122	2.94701	1.87772
O	-0.57152	3.90579	0.07848
P	-3.05114	-0.97933	1.29696
P	-2.96657	1.69422	-0.45534
C	-0.16922	0.04248	2.26690
C	-4.62761	-0.37162	0.50533
C	-4.31307	0.42525	-0.76350
C	2.30295	1.21582	-0.49570
C	0.80104	3.33021	3.18223
C	0.19195	5.05781	-0.27498
C	-0.74279	6.20540	-0.61293
C	3.07014	1.18414	-1.80570
C	2.00764	3.30457	4.10399
H	-5.21232	0.89209	-1.16293
H	-3.93505	-0.24331	-1.53853
H	-5.31537	-1.19006	0.29379
H	-5.11244	0.27120	1.24149
H	0.83363	4.82483	-1.12963
H	0.84896	5.33815	0.55382
H	1.91261	0.21627	-0.26754
H	2.96876	1.49914	0.32515
H	0.02460	2.65739	3.56602
H	0.36838	4.33816	3.16100
H	-1.38498	5.94820	-1.45705
H	-0.17215	7.09699	-0.88072
H	-1.37966	6.44967	0.23855
H	2.41751	0.88724	-2.62785
H	3.89759	0.47385	-1.74810
H	3.47717	2.16977	-2.03449
H	2.42302	2.29808	4.15860
H	1.72842	3.61970	5.11172
H	2.78459	3.97513	3.73495
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C	-2.56516	-2.51068	0.30381
C	-5.28849	3.44591	-0.38428
C	-3.81174	3.38715	1.65643
C	-3.87848	-0.34666	3.89751
C	-2.30806	2.07835	-2.16684
C	-1.50827	0.87870	-2.70377
C	-1.58807	-3.39094	1.10364
C	-3.69574	-3.34658	-0.31900
C	-3.57017	-1.56179	3.00382
C	-4.71303	-2.58826	3.06181
H	-5.64579	4.44308	-0.09764
H	-5.38462	3.36225	-1.47008
H	-5.97312	2.71968	0.07091
H	-3.21027	4.04577	-0.28772
H	-4.18269	4.37720	1.95129
H	-2.79712	3.26583	2.04422
H	-4.45193	2.64001	2.14156
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H	-3.25984	-4.14913	-0.92773
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H	-4.01806	-0.67413	4.93509
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H	-0.99810	1.16315	-3.63209
H	-2.15653	0.02457	-2.93910
H	-0.74883	0.55514	-1.98575
H	-3.80483	3.51156	-2.90666
H	-4.12623	1.83112	-3.38072
H	-2.83024	2.74238	-4.15922
H	-1.59698	2.88678	-1.96237

SCF Energy = −2212.49663225