Electronic Supplementary Material (ESI) for Dalton Transactions.

Density Functional Theory Calculations of Rh-β-diketonato complexes

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Electronic Supplementary Information

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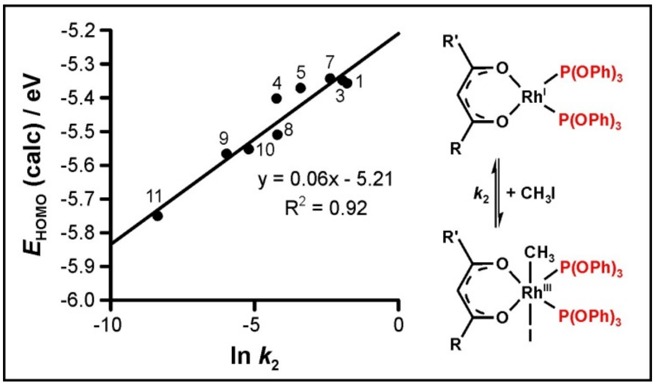

Figure S 1. Linear relationship between B3LYP/GTO-TZP (DZ on Rh) calculated E_{HOMO} of [Rh(β-diketonato)(P(OPh$_3$)$_3$)$_2$] and the experimental kinetic rate constant, k_2 (k_2 in dm^{3}mol^{-1}s^{-1}), of the [Rh(β-diketonato)(P(OPh)$_3$)$_2$] + CH$_3$I reaction. Complex numbering is according to Figure 1. Data was obtained from J. Conradie, "Oxidation potential of [Rh(β-diketonato)(P(OPh)$_3$)$_2$] complexes – relationships with experimental, electronic and calculated parameters", *Electrochimica Acta,* 2013, **110**, 718-725.

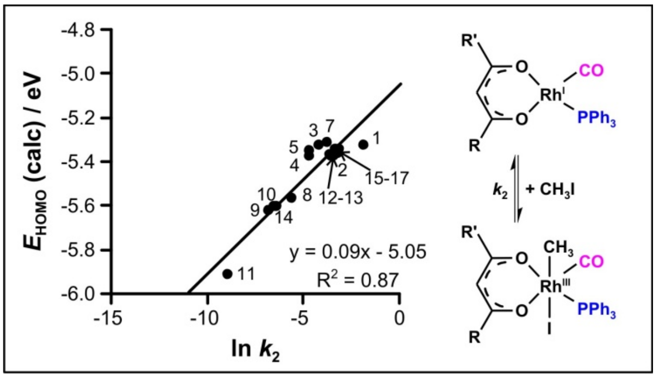

Figure S 2. Linear relationship between B3LYP/GTO-TZP (DZ on Rh) calculated E_{HOMO} and the experimental kinetic rate constant, k_2 (in dm^{3}mol^{-1}s^{-1}) of the CH$_3$I oxidative addition to [Rh(β-diketonato)(CO)(PPh$_3$)]. Note k_2 in this graph corresponds to k_1 in Scheme 2. Complex numbering is according to Figure 1 (for complexes 1-14), and further R, R' = Ph, CH$_2$CH$_3$ (15); Ph, (CH$_2$)$_2$CH$_3$ (16); Ph, (CH$_2$)$_3$CH$_3$ (17). Data was compiled for this study, see Table S 6.

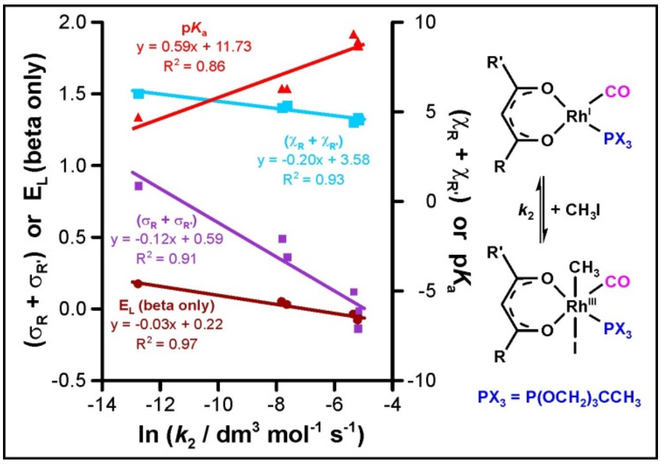

Figure S 3. Linear dependence of the empirical quantities ($\chi_R + \chi_{R'}$), ($\sigma_R + \sigma_{R'}$), pK_a and ΣE_L on the oxidative addition rate constant k_2 (in dm^{3}mol^{-1}s^{-1}) of the [Rh(β-diketonato)(CO)(P(OCH$_2$)$_3$CCH$_3$)] + CH$_3$I reaction. Data was obtained from J.J.C. Erasmus and J. Conradie, "Chemical and electrochemical oxidation of [Rh(β-diketonato)(CO)(P(OCH$_2$)$_3$CCH$_3$)]: an experimental and DFT study", *Dalton Transactions*, 2013, **42**, 8655–8666.

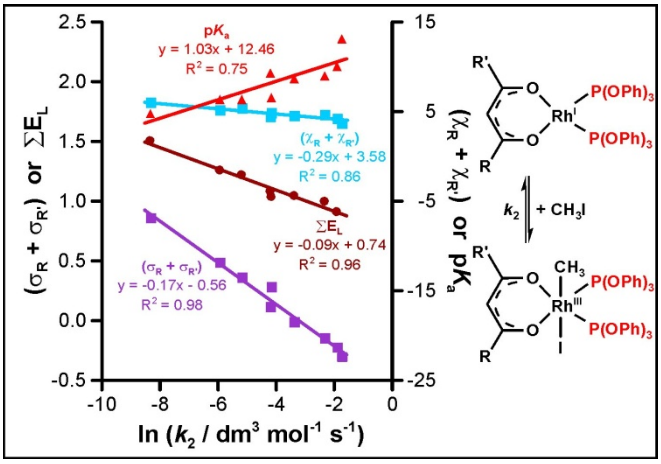

Figure S 4. Linear dependence of the empirical quantities ($\chi_R + \chi_{R'}$), ($\sigma_R + \sigma_{R'}$), pK_a and ΣE_L on the oxidative addition rate constant k_2 (in dm^{3}mol^{-1}s^{-1}) of the [Rh(β-diketonato)(P(OPh)$_3$)$_2$] + CH$_3$I reaction. Data was obtained from M.M. Conradie, J.J.C. Erasmus and J. Conradie, "Iodomethane oxidative addition to beta-Diketonatobis(triphenylphosphite)rhodium(I) complexes: A synthetic, kinetic and computational study", *Polyhedron*, 2011, **30**, 2345-2353; and from J. Conradie, "Oxidation potential of [Rh(β-diketonato)(P(OPh)$_3$)$_2$] complexes – relationships with experimental, electronic and calculated parameters", *Electrochimica Acta,* 2013, **110**, 718-725.

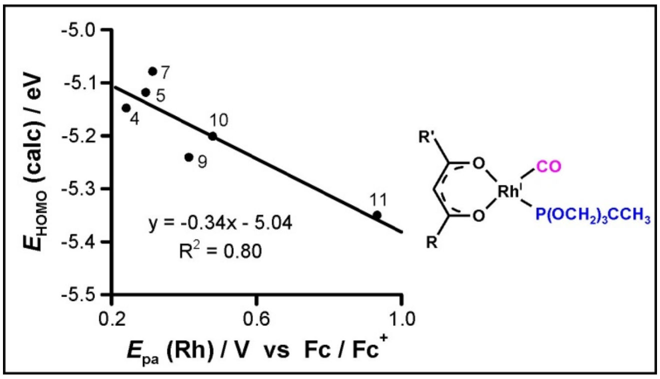

Figure S 5. Linear relationship between E_{HOMO} of [Rh(β-diketonato)(CO)(P(OCH$_2$)$_3$CCH$_3$)] and the experimental oxidation potential of rhodium, E_{pa}(Rh). Complex numbering is according to Figure 1. Data was obtained from reference J.J.C. Erasmus and J. Conradie, "Chemical and electrochemical oxidation of [Rh(β-diketonato)(CO)(P(OCH$_2$)$_3$CCH$_3$)]: an experimental and DFT study", *Dalton Transactions*, 2013, **42**, 8655–8666.

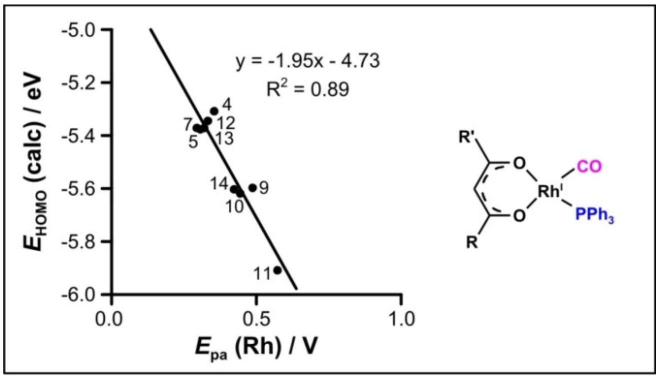

Figure S 6. Linear relationship between E_{HOMO} of [Rh(β-diketonato)(CO)(PPh$_3$)] and the experimental oxidation potential of rhodium, E_{pa}(Rh). Complex numbering is according to Figure 1. Data was obtained from reference H. Ferreira, M.M. Conradie and J. Conradie, "Electrochemical study of Carbonyl Phosphine β-Diketonato Rhodium(I) Complexes", *Electrochimica Acta*, 2013, **113**, 519-526.

Table S 1. The Gordy scale group electronegativities, χ_R,[1,2] used to quantify the electron donating properties of the R and R' groups of the β-diketones ($RCOCH_2COR'$). (Fc = ferrocenyl).

R group	χ_R	**Reference**
CF_3	3.01	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.,* 1998, 2507-2514.
Cl	2.97	R.E. Kagarise, *J. Am. Chem. Soc*., 1955, 77, 1377-1379.
Fc^+	2.82	W.C. du Plessis, J.J.C. Erasmus, G.J. Lamprecht, J. Conradie, T.S. Cameron, M.A.S. Aquino and J.C. Swarts, *Canadian J. Chem.*, 1999, **77**, 378-386.
CCl_3	2.76	R.E. Kagarise, *J. Am. Chem. Soc*., 1955, **77**, 1377-1379.
$CHCl_2$	2.62	R.E. Kagarise, *J. Am. Chem. Soc*., 1955, **77**, 1377-1379.
CH_3	2.34	R.E. Kagarise, *J. Am. Chem. Soc*., 1955, **77**, 1377-1379.
Ph	2.21	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.,* 1998, 2507-2514.
H	2.13	R.E. Kagarise, *J. Am. Chem. Soc*., 1955, **77**, 1377-1379.
Fc	1.87	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.,* 1998, 2507-2514.
CH_2Br	2.44	R.E. Kagarise, *J. Am. Chem. Soc*., 1955, **77**, 1377-1379.
CH_2Cl	2.48	R.E. Kagarise, *J. Am. Chem. Soc*., 1955, **77**, 1377-1379.
CH_2CH_3	2.31	N.F. Stuurman and J. Conradie, *J. Organomet. Chem*., 2009, **694**, 259-268.
$CH_2CH_2CH_3$	2.41	N.F. Stuurman and J. Conradie, *J. Organomet. Chem*., 2009, **694**, 259-268.
$CH_2CH_2CH_2CH_3$	2.22	N.F. Stuurman and J. Conradie, *J. Organomet. Chem*., 2009, **694**, 259-268.
C_4H_3S	2.10	M.M. Conradie, A.J. Muller and J. Conradie, *S. Afr. J. Chem.*, 2008, **61**, 13-21.

Table S 2. pK_a of the indicated β-diketones ($RCOCH_2COR'$), with side groups R and R'. (Fc = $(C_5H_5)Fe(C_5H_4)$ = ferrocenyl, and Rc = $(C_5H_5)Ru(C_5H_4)$ = ruthenocenyl).

R	**R'**	**pK_a**	**Ref pK_a**
C_4H_3S	C_4H_3S	8.893	M.M. Conradie, A.J. Muller and J. Conradie, *S. Afr. J. Chem.*, 2008, **61**, 13-21.
C_6H_5	C_4H_3S	9.006	M.M. Conradie, A.J. Muller and J. Conradie, *S. Afr. J. Chem.*, 2008, **61**, 13-21.
C_6H_5	C_6H_5	9.35	J. Starý, in *The Solvent Extraction of Metal Chelates*, MacMillan Company, New York, 1964, Appendix.
C_6H_5	CF_3	6.3	J. Starý, in *The Solvent Extraction of Metal Chelates*, MacMillan Company, New York, 1964, Appendix.
C_6H_5	$CH_2CH_2CH_2CH_3$	9.33	N.F. Stuurman and J. Conradie, *J. Organomet. Chem.*, 2009, **694**, 259-268.
C_6H_5	$CH_2CH_2CH_3$	9.23	N.F. Stuurman and J. Conradie, *J. Organomet. Chem.*, 2009, **694**, 259-268.
C_6H_5	CH_2CH_3	9.33	N.F. Stuurman and J. Conradie, *J. Organomet. Chem.*, 2009, **694**, 259-268.
C_6H_5	CH_3	8.70	J. Starý, in *The Solvent Extraction of Metal Chelates*, MacMillan Company, New York, 1964, Appendix.
CF_3	$C(CH_3)_3$	7.13	J. Conradie, *Chemical kinetics, electrochemistry and structural aspects of ferrocene-containing β-diketonato complexes of rhodium(I) and iridium(I)*, PhD Thesis, University of the Free State, R.S.A., 1999.
CF_3	C_4H_3S	6.497	M.M. Conradie, A.J. Muller and J. Conradie, *S. Afr. J. Chem.*, 2008, **61**, 13-21.
CF_3	CF_3	4.71	M. Ellinger, H. Duschner and K. Starke, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1063-1067.
CF_3	CF_3	5.24	J. Starý, in *The Solvent Extraction of Metal Chelates*, MacMillan Company, New York, 1964, Appendix.
CF_3	$CH(CH_3)_2$	6.80	G.J.J. Steyn, A. Roodt and J.G. Leipoldt, *Inorg. Chem.*, 1992, **31**, 3477-3481.
CF_3	CH_2CH_3	6.64	J. Conradie, *Chemical kinetics, electrochemistry and structural aspects of ferrocene-containing β-diketonato complexes of rhodium(I) and iridium(I)*, PhD Thesis, University of the Free State, R.S.A., 1999.
CF_3	CH_3	6.3	J. Starý, in *The Solvent Extraction of Metal Chelates*, MacMillan Company, New York, 1964, Appendix.
CH_3	CH_3	8.95	J. Starý, in *The Solvent Extraction of Metal Chelates*, MacMillan Company, New York, 1964, Appendix.
Fc	C_6H_5	10.41	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.*, 1998, 2507-2514.
Fc	CCl_3	7.13	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.*, 1998, 2507-2514.
Fc	CF_3	6.56	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.*, 1998, 2507-2514.
Fc	CH_3	10.01	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.*, 1998, 2507-2514.
Fc	Fc	13.1	W.C. du Plessis, T.G. Vosloo and J.C. Swarts, *J. Chem. Soc., Dalton Trans.*, 1998, 2507-2514.
Rc	C_6H_5	11.31	K.C. Kemp, E. Fourie, J. Conradie and J.C. Swarts, *Organometallics*, 2008, **27**, 353-362.
Rc	CF_3	7.36	K.C. Kemp, E. Fourie, J. Conradie and J.C. Swarts, *Organometallics*, 2008, **27**, 353-362.
Rc	CH_3	10.22	K.C. Kemp, E. Fourie, J. Conradie and J.C. Swarts, *Organometallics*, 2008, **27**, 353-362.
Rc	Fc	12.90	K.C. Kemp, E. Fourie, J. Conradie and J.C. Swarts, *Organometallics*, 2008, **27**, 353-362.
Rc	Rc	12.70	K.C. Kemp, E. Fourie, J. Conradie and J.C. Swarts, *Organometallics*, 2008, **27**, 353-362.

Table S 3. The sum of the Hammett meta-substituent constants[3,4] ($\sigma_R + \sigma_{R'}$), of the indicated free β-diketones ($RCOCH_2COR'$), with side groups R and R'. (Fc = ferrocenyl).

R	**R'**	**σ_R**	**$\sigma_{R'}$**	**($\sigma_R + \sigma_{R'}$)**
C_4H_3S	C_4H_3S	0.09	0.09	0.18
C_6H_5	C_4H_3S	0.06	0.09	0.15
C_6H_5	C_6H_5	0.06	0.06	0.12
C_6H_5	CF_3	0.06	0.43	0.49
C_6H_5	$CH_2CH_2CH_2CH_3$	0.06	-0.08	-0.02
C_6H_5	CH_2CH_3	0.06	-0.07	-0.01
C_6H_5	CH_3	0.06	-0.069	-0.01
CF_3	$C(CH_3)_3$	0.43	-0.10	0.33
CF_3	C_4H_3O	0.43	0.06	0.49
CF_3	C_4H_3S	0.43	0.09	0.52
CF_3	CF_3	0.43	0.43	0.86
CF_3	CH_2CH_3	0.43	-0.07	0.36
CF_3	CH_3	0.43	-0.069	0.36
CH_3	CH_3	-0.069	-0.069	-0.14
Fc	$C(CH_3)_3$	-0.15	-0.10	-0.25
Fc	C_6H_5	-0.15	0.06	-0.09
Fc	CCl_3	-0.15	0.40	0.25
Fc	CF_3	-0.15	0.43	0.28
Fc	CH_2CH_3	-0.15	-0.07	-0.22
Fc	CH_3	-0.15	-0.069	-0.22
Fc	Fc	-0.15	-0.15	-0.30
Fc	H	-0.15	0.00	-0.15

Values are from C. Hansch, A. Leo and R.W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.

Table S 4. The Lever electronic parameter, E_L, of the indicated β-diketonato ligands.[5,6,7,8] (Fc = ferrocenyl).

β-diketone	**E_L**	**Reference**
$CF_3COCH_2COCF_3$	0.17	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
$CH_3COCH_2COCF_3$	0.03	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
$C_6H_5COCH_2COCF_3$	0.05	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
$FcCOCH_2COCF_3$	-0.064	J.J.C. Erasmus and J. Conradie, *Electrochim. Acta*, 2011, **565**, 9287-9294.
$C_6H_5COCH_2COCH_3$	-0.06	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
$CH_3COCH_2COCH_3$	-0.08	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
$C_6H_5COCH_2COC_6H_6$	-0.04	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
$FcCOCH_2COCH_3$	-0.126	J.J.C. Erasmus and J. Conradie, *Electrochim. Acta*, 2011, **565**, 9287-9294.
$C_6H_5COCH_2COFc$	-0.118	J.J.C. Erasmus and J. Conradie, *Electrochim. Acta*, 2011, **565**, 9287-9294.
CO	0.99	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
PPh_3	0.39	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.
$P(OPh)_3$	0.58	A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271-1285.

Table S 5. Chemical oxidative addition kinetic data, electronic parameters and calculated HOMO energies for [Rh(RCOCHCOR')(P(OPh$_3$)$_2$)] complexes. Complex numbering is according to Figure 1.

	E_{HOMO} / eV (B3LYP) [a]	E_{HOMO} / eV (PW91) [b]	pK_a [c]	$\chi_R + \chi_{R'}$ [d]	$\sigma_R + \sigma_{R'}$ [e]	E_L [f]	k_2/ (mol^{-1} dm^3 s^{-1}) [g]	E_{pa}(Rh) [h]
1	-5.358	[i]	13.1	3.74	-0.30		0.177	0.124
2	-5.370	[i]	10.41	4.08	-0.09	0.92	-	0.173
3	-5.350	-4.360	10.01	4.21	-0.22	0.91	0.151	0.176
4	-5.403	-4.457	9.35	4.42	0.12	1.08	0.0149	0.324
5	-5.372	-4.414	8.7	4.55	-0.01	1.04	0.0342	0.322
7	-5.345	-4.342	8.95	4.68	-0.14	1.00	0.096	0.308
8	-5.510	-4.531	6.56	4.88	0.28	1.03	0.0155	0.312
9	-5.569	-4.595	6.3	5.22	0.49	1.26	0.00263	0.461
10	-5.554	-4.549	6.3	5.35	0.36	1.22	0.0056	0.477
11	-5.752	-4.774	4.71	6.02	0.86	1.50	0.00024	0.881

a DFT B3LYP/GTO-TZP (DZ on Rh) calculations with the Gaussian 09 programme package. See DFT calculations – methods below for details.

b DFT PW91/STO-TZ2P calculations with the ADF (Amsterdam Density Functional) 2013 program. See DFT calculations – methods below for details.

c From Table S2

d From Table S3

e From Table S1

f Lever electrochemical ligand parameter E_L of the β-diketonato ligand only, From Table S4

g Kinetic data from Reference [9]

h E_{pa}(Rh) *vs* Fc/Fc$^+$/V from reference [10]

i The HOMO is on Fe, instead of Rh, and therefore not included.

Table S 6. Chemical oxidative addition kinetic data, electronic parameters and calculated HOMO energies for [Rh(RCOCHCOR')(CO)(PPh$_3$)] complexes. Complex numbering is according to Figure 1 (for complexes 1-14), and further R, R' = Ph, CH$_2$CH$_3$ (15); Ph, (CH$_2$)$_2$CH$_3$ (16); Ph, (CH$_2$)$_3$CH$_3$ (17).

Complex	E_{HOMO} / eV (B3LYP) [a]	E_{HOMO} / eV (PW91) [b]	pK_a (free β-diketone) [c]	$\chi_R + \chi_{R'}$ [d]	$\sigma_R + \sigma_{R'}$ [e]	Σ E_L [f]	k_2 / (mol^{-1} dm^3 s^{-1}) [g]
1	-5.323	[i]	13.1	3.74	-0.3		0.155
2	-5.360	[i]	10.41	4.08	-0.09	1.14	0.0409
3	-5.324	-4.368	10.01	4.21	-0.22	1.13	0.0155
4	-5.378	-4.516	9.35	4.42	0.12	1.30	0.00961
5	-5.348	-4.455	8.7	4.55	-0.01	1.26	0.0093
7	-5.311	-4.400	8.95	4.68	-0.14	1.22	0.024
8	-5.567	[i]	6.56	4.88	0.28	1.25	0.0037
9	-5.620	-4.743	6.3	5.22	0.49	1.48	0.00112
10	-5.602	-4.694	6.3	5.35	0.36	1.44	0.00146
11	-5.912	-5.023	4.71	6.02	0.86	1.72	0.00013
12	-5.373	-4.476	8.893	4.2	0.18		0.029
13	-5.371	-4.503	9.006	4.31	0.15		0.0265
14	-5.606	-4.726	6.497	5.11	0.52		0.00171
15	-5.376	-4.463	9.33	4.52	-0.01		0.0333
16	-5.343	-4.500	9.33	4.43	-0.02		0.0354
17	-5.347	-4.445	9.23	4.62			0.0437

a DFT B3LYP/GTO-TZP (DZ on Rh) calculations with the Gaussian 09 programme package. See DFT calculations – methods below for details.

b DFT PW91/STO-TZ2P calculations with the ADF (Amsterdam Density Functional) 2013 program. See DFT See DFT calculations – methods below for details.

c From Table S2

d From Table S3

e From Table S1

f Σ E_L = 2 x E_L (β-diketone) + E_L (CO) + E_L (PPh$_3$); From Table S4

g Kinetic data from Reference [11]

i HOMO is on Fe, instead of Rh, and therefore not included.

Table S 7. Chemical oxidative addition kinetic data, electronic parameters and calculated HOMO energies for [Rh(β-diketonato)(CO)(P(OCH$_2$)$_3$CCH$_3$)] complexes. Complex numbering is according to Figure 1.

Complex	**E_{HOMO} / eV (PW91)** [b]	**pK_a (free β-diketone)** [c]	**$\chi_R + \chi_{R'}$** [d]	**$\sigma_R + \sigma_{R'}$** [e]	**E_L** [f]	**k_2 / (mol^{-1} dm^3 s^{-1})** [g]
4	-4.643	9.35	4.42	0.12	-0.04	0.00481
5	-4.582	8.7	4.55	-0.01	-0.06	0.00563
7	-4.490	8.95	4.68	-0.14	-0.08	0.00554
9	-4.894	6.3	5.22	0.49	0.05	0.000409
10	-4.835	6.3	5.35	0.36	0.03	0.000480
11	-5.205	4.71	6.02	0.86	0.17	0.0000029

b DFT PW91/STO-TZ2P calculations with the ADF (Amsterdam Density Functional) 2013 program. See DFT See DFT calculations – methods below for details.
c From Table S2
d From Table S3
e From Table S1
f Lever electrochemical ligand parameter E_L of the β-diketonato ligand only, From Table S4
g Kinetic data from Reference [12]

DFT calculations - methods

2. [Rh(β-diketonato)(CO)$_2$] complexes

"All calculations were performed with the hybrid functional B3LYP,[13] as implemented in the Gaussian 03 program package.[14] Geometries were optimized in the gas phase, with the triple-ζ basis set 6-311G(d,p) on all atoms except rhodium, where we used LANL2DZ (corresponding to the Los Alamos Effective Core Potential plus DZ[15])." [16]

3. [Rh(β-diketonato)(cod)] complexes

Density Functional Theory calculations were carried out in the gas phase, using the ADF (Amsterdam Density Functional) 2013 programme,[17] with the GGA (Generalised Gradient Approximation) functional PW91 (Perdew-Wang, 1991).[18] The TZ2P (Triple ζ polarised) basis set, with a fine mesh for numerical integration, a spin-restricted formalism and full geometry optimization with tight convergence criteria, as implemented in the ADF 2013 program, was used for minimum energy searches. Scalar relativistic effects were used with the ZORA[19] formalism (Zero Order Regular Approximation).

4. [Rh(β-diketonato)(P(OPh$_3$))$_2$] complexes

"DFT calculations were carried out using the ADF (Amsterdam Density Functional) 2007 programme,[16] with the GGA (Generalised Gradient Approximation) functional PW91 (Perdew-Wang, 1991).[17] The TZP (Triple ζ polarised) basis set, with a fine mesh for numerical integration, a spin-restricted formalism and full geometry optimization with tight convergence criteria, was used for minimum energy and transition state (TS) searches. Approximate structures of the TS have been determined with linear transit (LT) scans, with a constrained optimization along a chosen reaction coordinate, to sketch an approximate path over the TS between reactants and products. Throughout, all calculations have been performed with no symmetry constraint (C_1) and all structures have been calculated as singlet states.

Numerical frequency analyses,[20] where the frequencies are computed numerically by differentiation of energy gradients in slightly displaced geometries, have been performed to verify the TS geometries. A TS has one imaginary frequency.

Zero point energy and thermal corrections (vibrational, rotational and translational) were made in the calculation of the thermodynamic parameters. The enthalpy (H) and Gibbs free energy (G) were calculated from

$$\mathrm{U} = \mathrm{E}_{\mathrm{TBE}} + \mathrm{E}_{\mathrm{ZPE}} + \mathrm{E}_{\mathrm{IE}} \quad (1)$$

$$H = \mathrm{U} + \mathrm{RT} \quad (2)$$

$$G = H - \mathrm{T}S \quad (3)$$

where U is the total energy, $\mathrm{E}_{\mathrm{TBE}}$ is total bonding energy, $\mathrm{E}_{\mathrm{ZPE}}$ is zero point energy, E_{IE} is internal energy, R is the gas constant, T is temperature and S is entropy. The entropy (S) was calculated from the temperature dependent partition function in ADF at 298.15 K. The computed results assume an ideal gas.

Solvent effects were taken into account for all calculations reported here. The COSMO (Conductor like Screening Model) model of solvation[21] was used as implemented in ADF.[22] The COSMO model is a dielectric model in which the solute molecule is embedded in a molecule-shaped cavity surrounded by a dielectric medium with a given dielectric constant (ε_0). The type of cavity used is Esurf[23] and the solvent used is methanol ($\varepsilon_0 = 32.6$). Where applicable, scalar relativistic effects were used with the ZORA[18] (Zero Order Regular Approximation) formalism."[24]

5. [Rh(β-diketonato)(CO)(PX_3)] complexes, where PX_3 = PPh_3, ($P(OCH_2)_3CCH_3$), or other tertiary phosphines

DFT calculations related to the conformational preferences of PPh_3-containing Rh-complexes and the oxidative addition of methyl iodide to [Rh(acac)(CO)(PPh_3)] "were carried out using the ADF (Amsterdam Density Functional) 2009 programme[16] with the GGA (Generalized Gradient Approximation) functional PW91.[17] The TZP (Triple ζ polarized) basis set, with a fine mesh for numerical integration, a spin-restricted formalism and a full geometry optimization with tight convergence criteria, was used for minimum energy and transition state (TS) searches. Approximate structures of the TS have been determined with linear transit (LT) scans, with a constraint optimization along a chosen reaction coordinate, to sketch an approximate path over the TS between reactants and products. Numerical frequency analyses,[19] where the frequencies are computed numerically by differentiation of energy gradients in slightly displaced geometries, have been performed to verify the TS geometries. A TS has one imaginary frequency. Finally, the TS was allowed to relax after displacing the atoms according to the reaction coordinate as determined by the eigenvectors. Throughout, all calculations have been performed with no symmetry constraint (C_1) and all structures have been calculated as singlet states."[25]

Calculations related to the the orientation of PPh_3 in a series of [Rh(β-diketonato)(CO)(PPh_3)] complexes was done in the gas phase, while the oxidative addition reaction [Rh(acac)(CO)(PPh_3)] + CH_3I was done in methanol as solvent: "Solvent effects were taken into account for all optimized structures reported here. The COSMO (Conductor like Screening Model) model of solvation[20] was used as implemented[21] in ADF. The COSMO model is a dielectric model in which the solute molecule is embedded in a molecule-shaped cavity surrounded by a dielectric medium with a given dielectric constant (ε_0). The type of cavity used is Esurf[22] and the solvent used is methanol (ε_0 = 32.6). [24]

6. DFT and chemical kinetics (for oxidative addition and substitution reactions) and
7. DFT and electrochemical oxidation

Figures 13, 14, 16, 17, 18, 20, 21: Density Functional Theory calculations were carried out in the gas phase using the ADF (Amsterdam Density Functional) 2013 programme,[16] with the GGA (Generalised Gradient Approximation) functional PW91 (Perdew-Wang, 1991).[17] The TZ2P (Triple ζ polarised) basis set, with a fine mesh for numerical integration, a spin-restricted formalism and full geometry optimization with tight convergence criteria, as implemented in the ADF 2013 program, was used for minimum energy searches. Scalar relativistic effects were used with the ZORA[18] formalism (Zero Order Regular Approximation).

Figures S1, S2, 19: "Calculations were performed with the Gaussian 09 programme package.[26] Geometries were optimized with the hybrid DFT functional B3LYP, which is composed of the Becke 88 exchange functional, in combination with the LYP correlation functional.[12] Optimizations were done in the gas phase with the triple-ζ basis set 6-311G(d,p) on all atoms except rhodium. The LANL2DZ basis set,[14] corresponding to the Los Alamos ECP plus DZ, was used for rhodium." [27]

References

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[1] Gordy scale group electronegativities, χ_R, are empirical numbers that express the combined tendency of not only one atom, but of a group of atoms, like R = CF_3 or CH_3, to attract electrons including those in a covalent bond, as a function of the number of valence electrons, n, and the covalent radius, r in Å, of atom groups, as discussed in: (a) P.R. Wells, in *Progress in Physical Organic Chemistry*, John Wiley & Sons Inc., New York, 1968, vol. 6, pp. 111-145; (b) R.E. Kagarise, 1955, *J. Am. Chem. Soc.*, 1955, **77**, 1377–1379.

[2] A. Kuhn, K.G. von Eschwege and J. Conradie, *Electrochim. Acta*, 2011, **56**, 6211-6218.

[3] L.P. Hammett, *Chem. Rev.*, 1935, **17**, 125–136.

[4] C. Hansch, A. Leo and R.W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.

[5] A.B.P. Lever, *Inorg. Chem.*, 1990, **29**, 1271–1285.

[6] M.F.C. Guedes da Silva, A.M. Trzeciak, J.J. Ziółkowski and A.J.L. Pombeiro, *J. Organomet. Chem.*, 2001, **620**, 174–181.

[7] A.M. Trzeciak, B. Borak, Z. Ciunik, J.J. Ziółkowski, M.F.C. Guedes da Silva and A.J.L. Pombeiro, *Eur. J. Inorg. Chem.*, 2004, 1411–1419.

[8] I. Kovacik, O. Gevert, H. Werner, M. Schmittel and R. Söllner, *Inorg. Chim. Acta*, 1998, **435**, 275–276.

[9] M.M. Conradie, J.J.C. Erasmus and J. Conradie, *Polyhedron*, 2011, **30**, 2345-2353.

[10] J.J.C. Erasmus and J. Conradie, Electrochim. Acta 2011, **56**, 9287-9294.

[11] Selected examples: (a) S.S. Basson, J.G. Leipoldt and J.T. Nel, *Inorg. Chim. Acta,* 1984, **84**, 167-172; (b) S.S. Basson, J.G. Leipoldt, A. Roodt, J.A. Venter and T.J. van der Walt, *Inorg. Chim. Acta,* 1986, **119**, 35-38; (c) J. Conradie, G.J. Lamprecht, A. Roodt and J.C. Swarts, *Polyhedron*, 2007, **26**, 5075-5087; (d) J. Conradie and J.C. Swarts, *Organometallics*, 2009, **28**, 1018-1026; (e) M.M. Conradie and J. Conradie, *Inorg. Chim. Acta,* 2008, **361**, 208-218; (f) M.M. Conradie and J. Conradie, *Inorg. Chim. Acta,* 2008, **361** , 2285-2295.

[12] J.J.C. Erasmus and J. Conradie, *Dalton Trans.*, 2013, **42**, 8655–8666.

[13] Selected examples: (a) A.D. Becke, *Phys. Rev.*, 1988, **A 38**, 3098-3100; (b) C. Lee, W. Yang and R.G. Parr, *Phys. Rev.*, 1988, **B 37**, 785-789.

[14] Gaussian 03, Revision E.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, 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, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, *Gaussian, Inc., Wallingford CT*, **2004**.

[15] Selected examples: (a) T.H. Dunning and P.J. Hay, in *Modern Theoretical Chemistry*, ed. H.F. Schaefer III, Plenum, New York, 1976, vol. 3, pp. 1-28; (b) P.J. Hay and W.R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283; (c) P.J. Hay and W.R. Wadt, *J. Chem. Phys*., 1985, **82**, 284-298; (d) P.J. Hay and W.R. Wadt, *J. Chem. Phys*., 1985, **82**, 299-311.

[16] K.H. Hopmann, N.F. Stuurman, A. Muller and J. Conradie, *Organometallics*, 2010, **29**, 2446–2458.

[17] Selected examples: (a) ADF 2008.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, 2008, http://www.scm.com; (b) G. Te Velde, F.M. Bickelhaupt, E.J. Baerends, C.F. Guerra, S.J.A. Van Gisbergen, J.G. Snijders and T. Ziegler, *J. Comput. Chem.,* 2001, ***22***, 931-967; (c) C. Fonseca Guerra, J.G. Snijders, G. te Velde and E.J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391-403.

[18] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671-6687. (Erratum: J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Perderson, D.J. Singh and C. Fiolhais, *Phys. Rev. B*, 1993, **48**, 4978).

[19] ZORA (Zero Order Regular Approximation) is described in: (a) E. van Lenthe, A.E. Ehlers and E.J. Baerends, *J. Chem. Phys.,* 1999, **110**, 8943-8953; (b) E. van Lenthe, E.J. Baerends and J.G. Snijders, *J. Chem. Phys.,* 1993, **99**, 4597-4610; (c) E. van Lenthe, E.J. Baerends and J.G. Snijders, *J. Chem. Phys.,* 1994, **101**, 9783-9792; (d) E. van Lenthe, J.G. Snijders and E.J. Baerends, *J. Chem. Phys.,* 1996, **105**, 6505-6516; (e) E. van Lenthe, R. van Leeuwen, E.J. Baerends and J.G. Snijders, *Int. J. Quantum Chem.,* 1996, **57**, 281-293.

[20] Selected examples: (a) L. Fan and T. Ziegler, *J. Chem. Phys.,* 1992, **96**, 9005-9012; (b) L. Fan and T. Ziegler, *J. Amer. Chem. Soc.*, 1992, **114**, 10890-10897.

[21] COSMO (Conductor like Screening Model) is described in: (a) A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799-805; (b) A. Klamt, *J. Phys. Chem.*, 1995, **99**, 2224-2235; (c) A. Klamt and V. Jones, *J. Chem. Phys.*, 1996, **105**, 9972-9981.

[22] C.C. Pye and T. Ziegler, *Theor. Chem. Acc.*, 1999, **101**, 396-408.

[23] J.L. Pascual-Ahuir, E. Silla and I. Tuñon, *J. Comput. Chem.*, 1994, **15**, 1127-1138.

[24] M.M. Conradie and J. Conradie, *J. Organomet. Chem.*, 2010, **695**, 2126-2133.

[25] M.M. Conradie and J. Conradie, *Dalton Trans.*, 2011, **40**, 8226-8237.

[26] GAUSSIAN 09 (Revision B.01), M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, 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, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian Inc., Wallingford, CT, 2010.

[27] J. Conradie, *Electrochim. Acta*, 2013, **110**, 718-725.