Supporting Information

CO-Induced Methyl Migration in a Rhodium Thiophosphoryl Pincer Complex and its Comparison with Phosphine-Based Complexes: The Divergent Effects of S and P Donor Ligands

Michael Montag,[*,†] Irena Efremenko,[‡] Gregory Leitus,[§] Yehoshoa Ben-David,[‡] Jan M. L. Martin,[‡] David Milstein[*,‡]

Part I: Experimental ^{1}H and ^{31}P NMR spectra of the SCS complexes (p. 1-14)

Part II: Computed atomic properties for SCS and PCP complexes (p. 15-42)

† Dr. M. Montag
Department of Biological Chemistry
Ariel University
Ariel 40700, Israel
Fax: (+972)3-906-6634
E-mail: michaelmo@ariel.ac.il

‡ Dr. I. Efremenko, Y. Ben-David, Prof. J. M. L. Martin, Prof. D. Milstein
Department of Organic Chemistry
Weizmann Institute of Science
Rehovot 76000, Israel
Fax: (+972)8-934-4142
E-mail: david.milstein@weizmann.ac.il

§ Dr. G. Leitus
Department of Chemical Research Support
Weizmann Institute of Science
Rehovot 76000, Israel

<u>Part I</u>: Experimental ^{1}H and ^{31}P NMR spectra of the SCS complexes

Complex 3

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_3CN): 87.67 (d, $^{2}J_{RhP}$ = 1.4 Hz). ^{1}H NMR (400 MHz, CD_3CN): 7.37 (m, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar–H), 7.20 (m, $^{3}J_{HH}$ = 7.7 Hz, 1H, Ar–H), 2.62 (m, $^{3}J_{HH}$ = 7.0 Hz, 2H, PC*H*$(CH_3)_2$), 2.56 (m, $^{3}J_{HH}$ = 7.0 Hz, 2H, PC*H*$(CH_3)_2$), 2.50 (s, 3H, COC*H*$_3$), 1.21 (dd, $^{3}J_{PH}$ = 17.8 Hz, $^{3}J_{HH}$ = 6.9 Hz, 6H, PCH(C*H*$_3)_2$), 1.21 (dd, $^{3}J_{PH}$ = 17.9 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, PCH(C*H*$_3)_2$), 1.10 (dd, $^{3}J_{PH}$ = 17.7 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, PCH(C*H*$_3)_2$), 1.09 (dd, $^{3}J_{PH}$ = 18.0 Hz, $^{3}J_{HH}$ = 7.1 Hz, 6H, PCH(C*H*$_3)_2$).

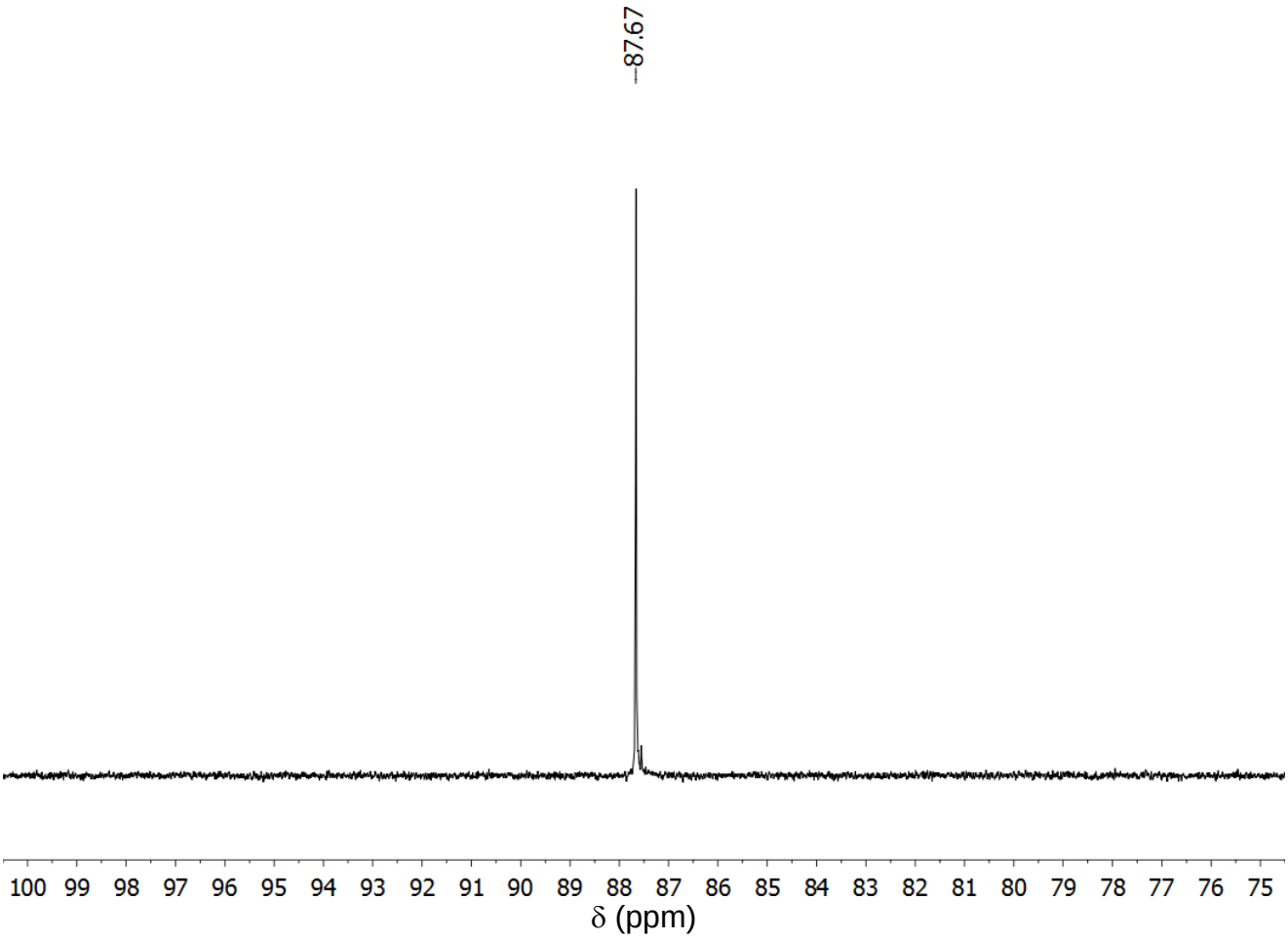


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** in CD_3CN at 20°C.

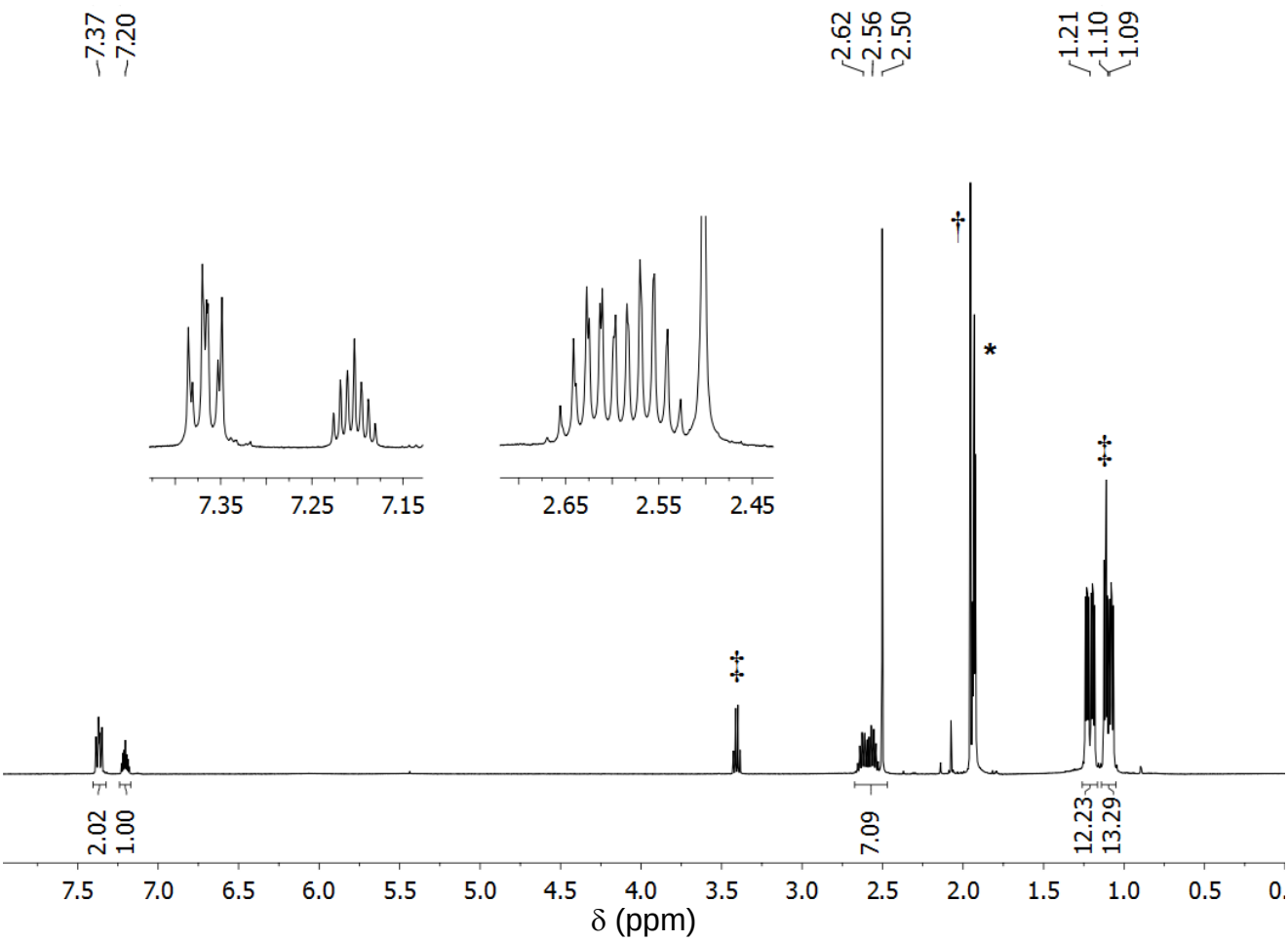


Figure S2. ^{1}H NMR spectrum of complex **3** in CD_3CN at 20°C. In addition to **3**, the following signals also appear in the spectrum: CHD_2CN from the solvent (*), CH_3CN from **3** (†), and residual ether (‡).

Complex 4

$^{31}P\{^{1}H\}$ NMR (202 MHz, acetone-d_6): 100.29 (d, $^{2}J_{RhP}$ = 2.8 Hz). ^{1}H NMR (500 MHz, acetone-d_6): 7.96 (m, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar–H), 7.57 (m, $^{3}J_{HH}$ = 7.6 Hz, 1H, Ar–H), 3.12 (m, $^{2}J_{PH}$ = $^{3}J_{HH}$ = 7.0 Hz, 2H, PC*H*$(CH_3)_2$), 2.81 (m, $^{2}J_{PH}$ = 8.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, 2H, PC*H*$(CH_3)_2$), 2.49 (s, 3H, COC*H*$_3$), 1.39 (dd, $^{3}J_{PH}$ = 18.2 Hz, $^{3}J_{HH}$ = 6.9 Hz, 6H, PCH(C*H*$_3)_2$), 1.28 (dd, $^{3}J_{PH}$ = 18.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, PCH(C*H*$_3)_2$), 1.19 (dd, $^{3}J_{PH}$ = 18.2 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, PCH(C*H*$_3)_2$), 1.13 (dd, $^{3}J_{PH}$ = 18.2 Hz, $^{3}J_{HH}$ = 7.1 Hz, 6H, PCH(C*H*$_3)_2$).

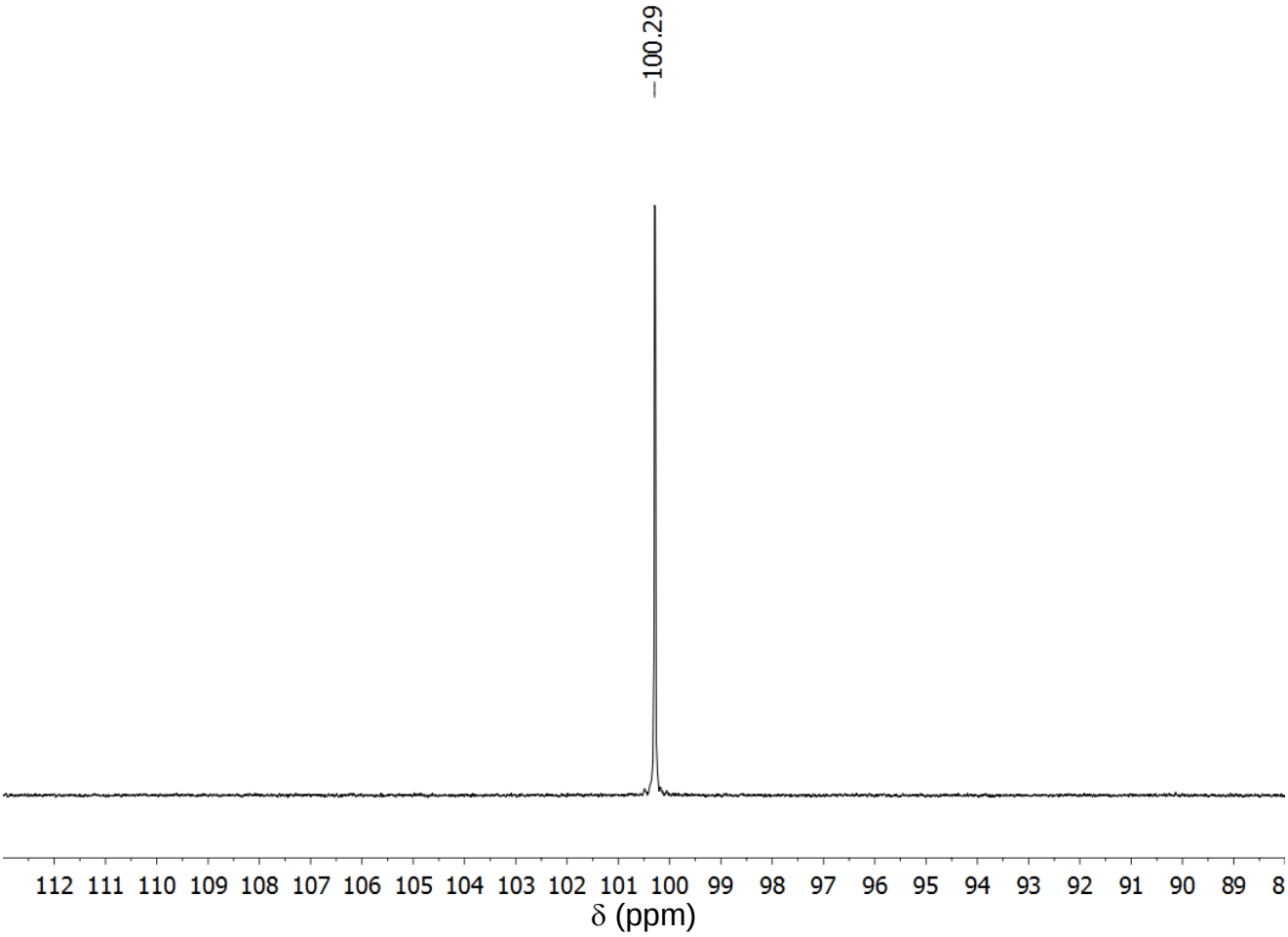


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of complex **4** in acetone-d_6 at 20°C.

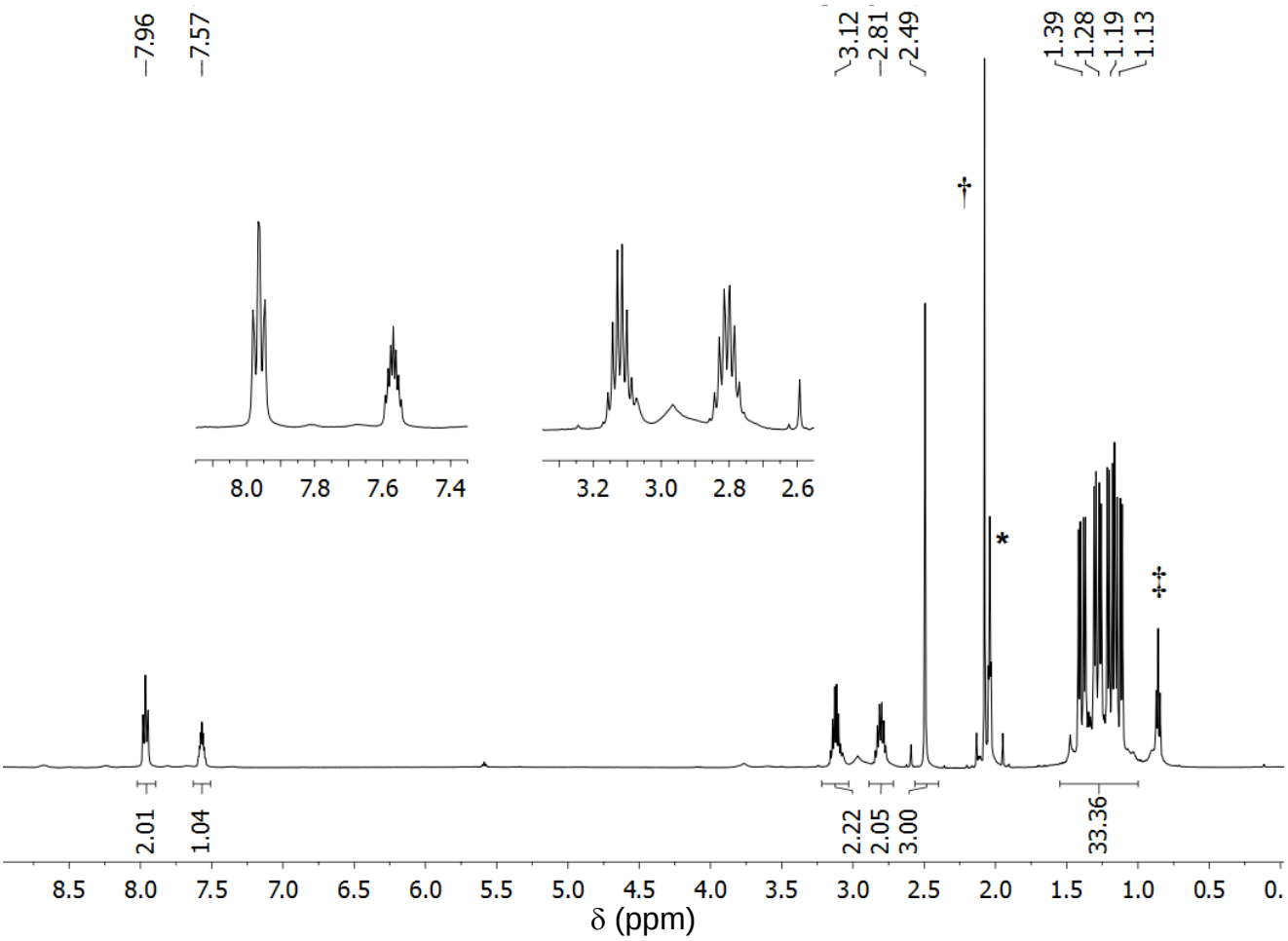


Figure S4. ^{1}H NMR spectrum of complex **4** in acetone-d_6 at 20°C. In addition to **4**, the following signals also appear in the spectrum: acetone-d_5 from the solvent (*), acetone from **4** (†), and residual pentane (‡).

Complex 6

$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_3CN): 87.72 (s). ^{1}H NMR (500 MHz, CD_3CN): 7.33 (m, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar–H), 7.16 (m, $^{3}J_{HH}$ = 7.7 Hz, 1H, Ar–H), 2.69 (m, $^{3}J_{HH}$ = 7.2 Hz, 2H, PC*H*$(CH_3)_2$), 2.47 (m, $^{3}J_{HH}$ = 7.2 Hz, 2H, PC*H*$(CH_3)_2$), 1.28 (dd, $^{3}J_{PH}$ = 17.6 Hz, $^{3}J_{HH}$ = 6.9 Hz, 6H, PCH(C*H*$_3)_2$), 1.17 (dd, $^{3}J_{PH}$ = 11.1 Hz, $^{3}J_{HH}$ = 7.3 Hz, 6H, PCH(C*H*$_3)_2$), 1.14 (dd, $^{3}J_{PH}$ = 10.7 Hz, $^{3}J_{HH}$ = 6.8 Hz, 6H, PCH(C*H*$_3)_2$), 1.05 (dd, $^{3}J_{PH}$ = 17.3 Hz, $^{3}J_{HH}$ = 7.2 Hz, 6H, PCH(C*H*$_3)_2$), -20.31 (dt, $^{1}J_{RhH}$ = 15.5 Hz, $^{3}J_{PH}$ = 1.6 Hz, 1H, Rh–H).

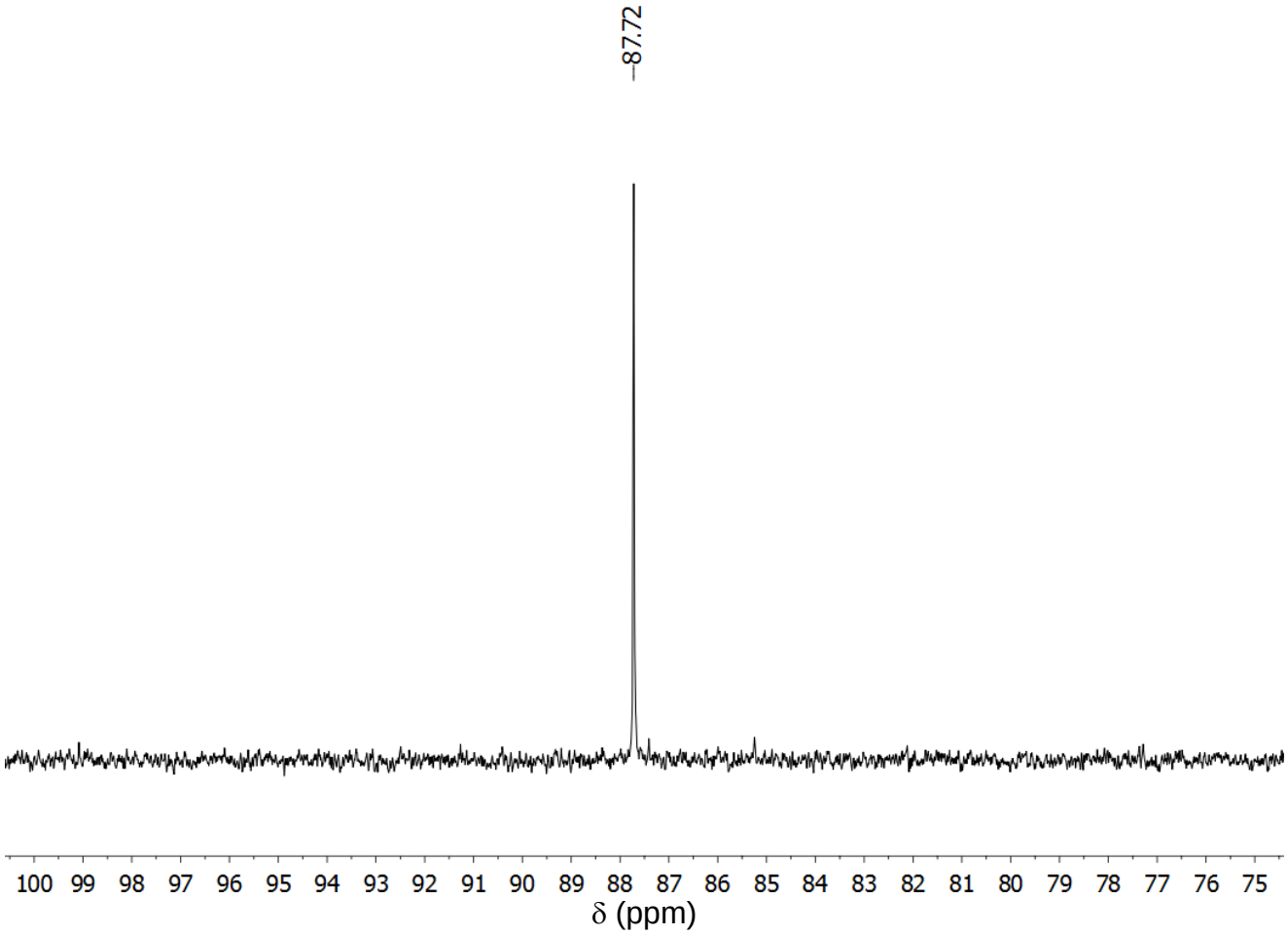


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6** in CD_3CN at 20°C.

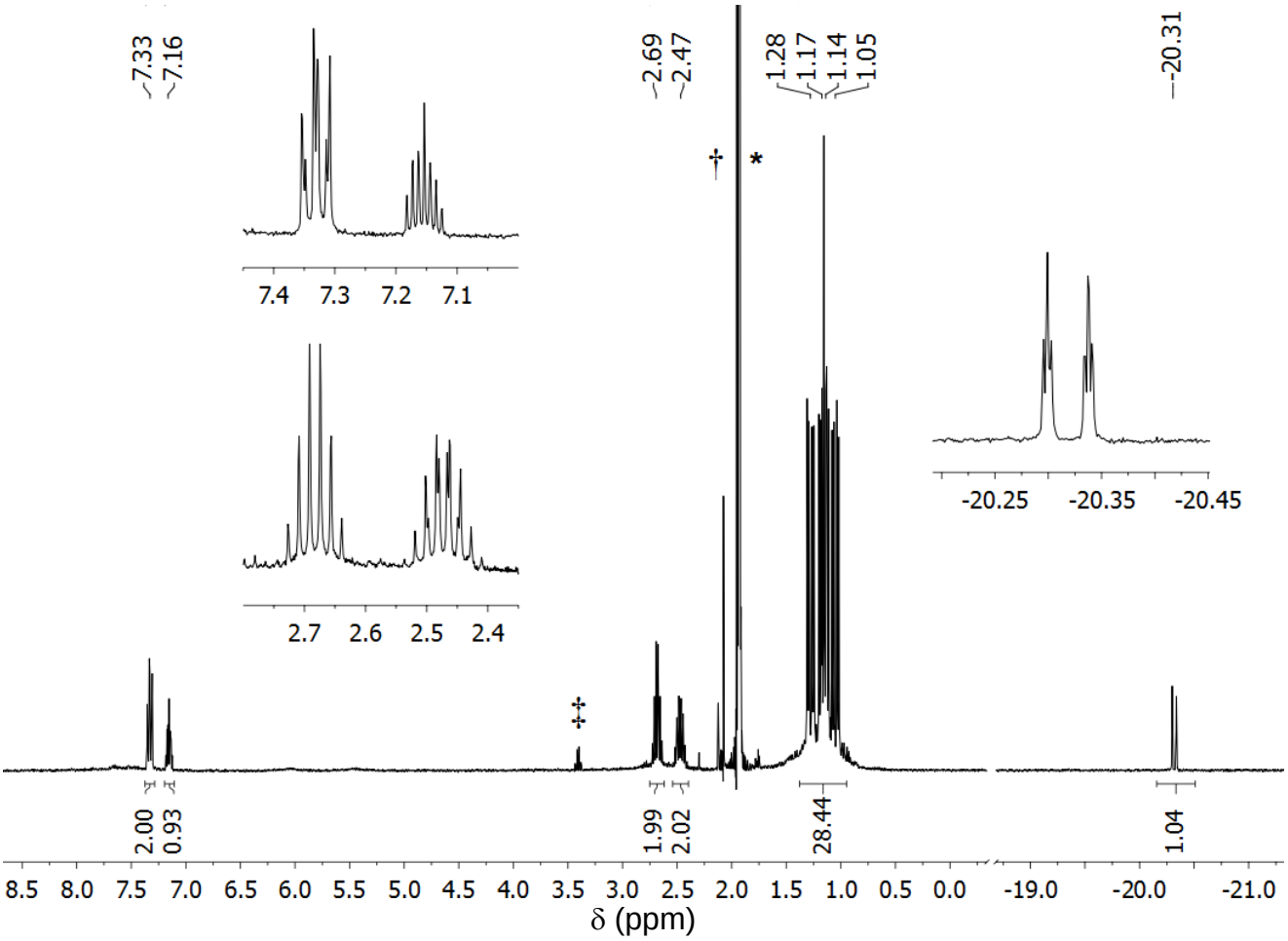


Figure S6. ^{1}H NMR spectrum of complex **6** in CD_3CN at 20°C. In addition to **6**, the following signals also appear in the spectrum: CHD_2CN from the solvent (*), CH_3CN from **6** (†), and residual ether (‡).

Complex 7

$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_3CN, 20°C): 77.29 (d, $^{3}J_{RhP}$ = 4.5 Hz). ^{1}H NMR (500 MHz, CD_3CN, 20°C): 6.82 (m, $^{3}J_{HH}$ = 7.5 Hz, 2H, Ar–H), 6.65 (m, $^{3}J_{HH}$ = 7.4 Hz, 1H, Ar–H), 2.40 (m, 4H, PC*H*$(CH_3)_2$), 1.30 (dd, $^{3}J_{PH}$ = 16.5 Hz, $^{3}J_{HH}$ = 7.1 Hz, 12H, PCH(C*H*$_3)_2$), 1.10 (dd, $^{3}J_{PH}$ = 16.6 Hz, $^{3}J_{HH}$ = 7.0 Hz, 12H, PCH(C*H*$_3)_2$).

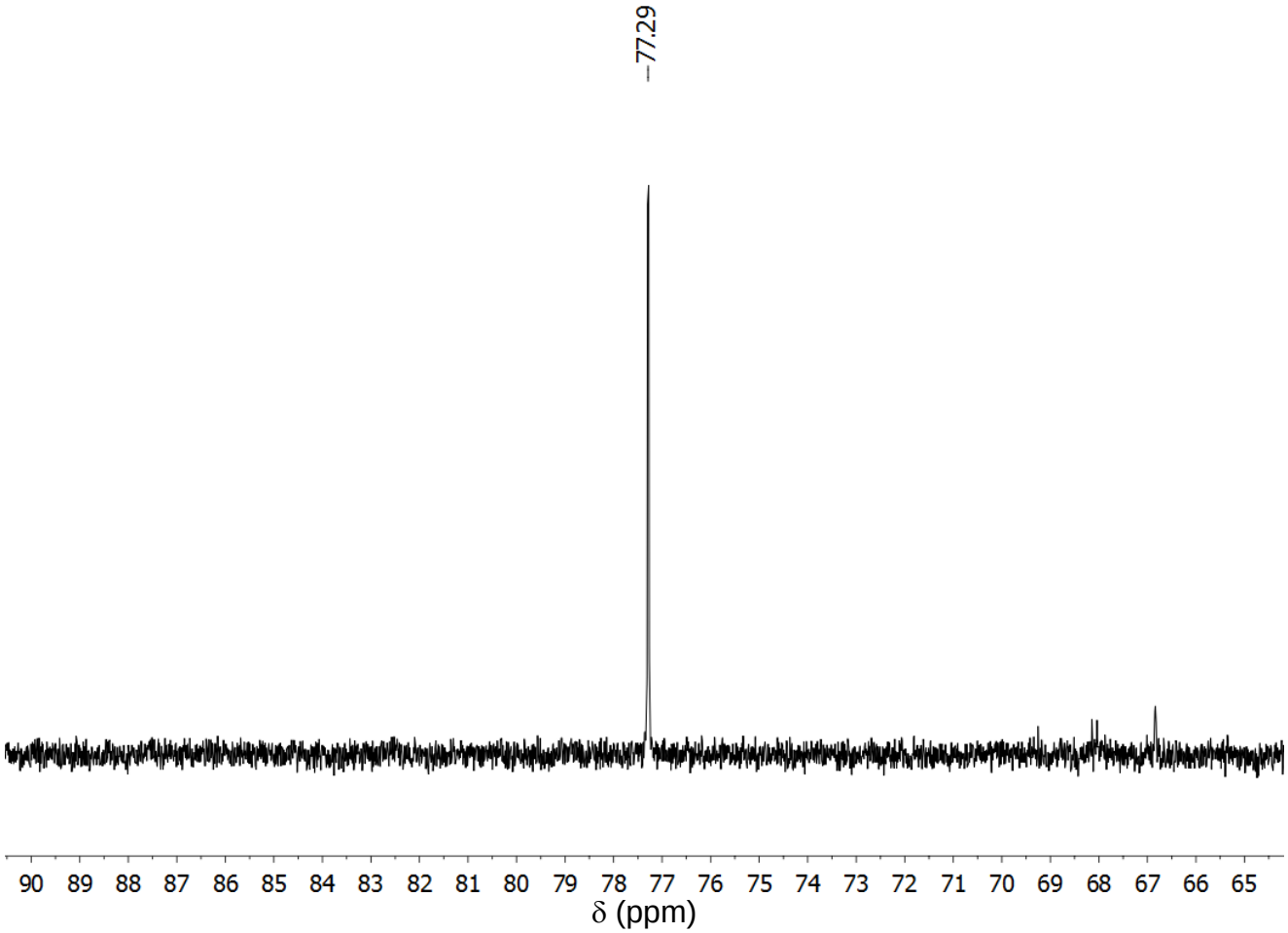


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of complex **7** in CD_3CN at 20°C.

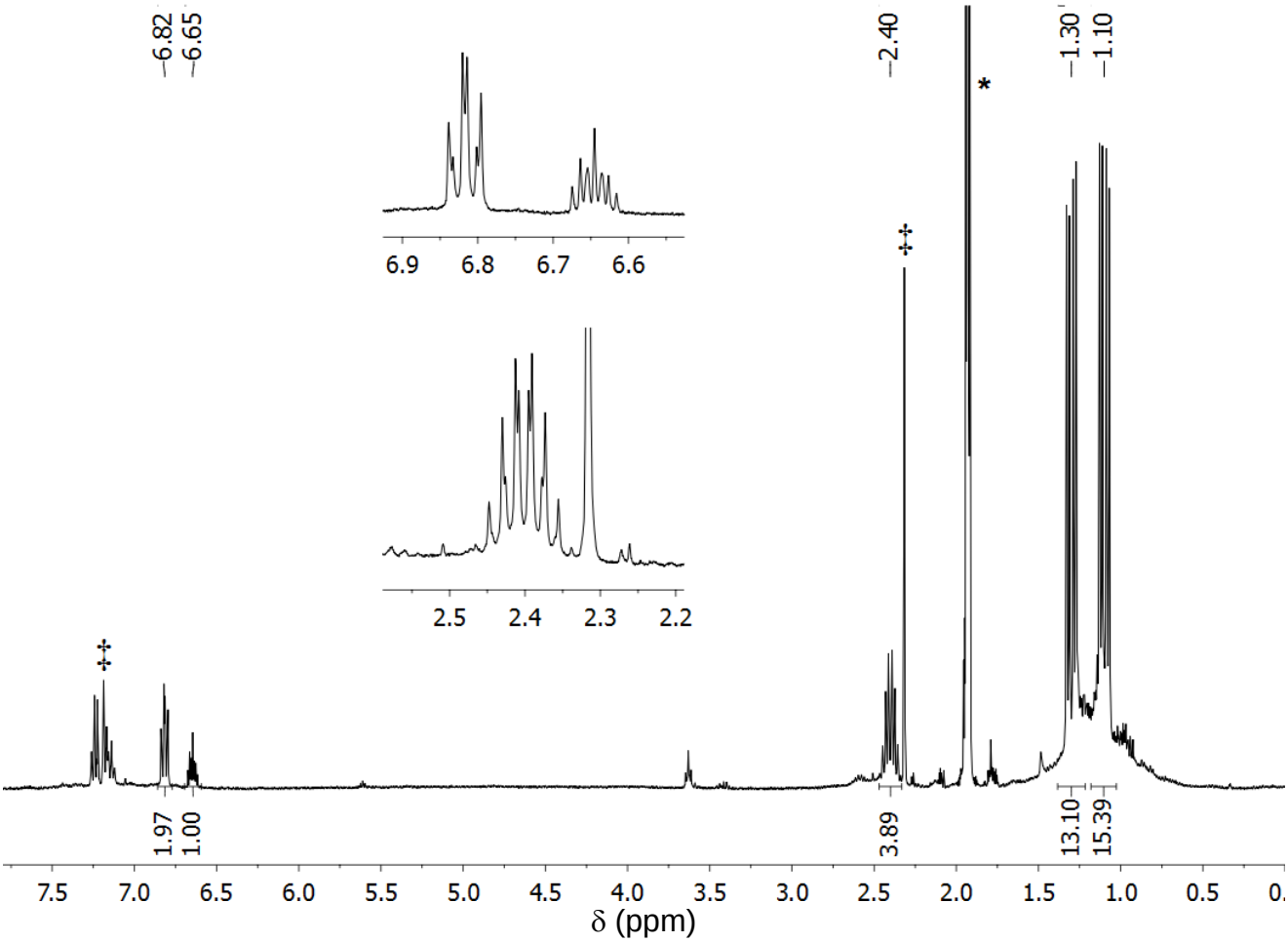


Figure S8. ^{1}H NMR spectrum of complex **7** in CD_3CN at 20°C. In addition to **7**, the following signals also appear in the spectrum: CHD_2CN from the solvent (*), and residual toluene (‡) from the extraction step of the synthesis. Toluene could not be thoroughly removed under vacuum due to decomposition of the complex under such conditions.

Complex 8

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 20°C): 98.33 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): 7.33 (m, $^{3}J_{HH}$ = 7.6 Hz, 2H, Ar–H), 7.12 (m, $^{3}J_{HH}$ = 7.6 Hz, 1H, Ar–H), 2.54 (m, $^{2}J_{PH} = {}^{3}J_{HH}$ = 7.0 Hz, 2H, PC*H*$(CH_3)_2$), 2.43 (m, $^{3}J_{HH}$ = 7.0 Hz, 2H, PC*H*$(CH_3)_2$), 1.69 (s, 3H, Rh–C*H*$_3$), 1.32 (dd, $^{3}J_{PH}$ = 17.5 Hz, $^{3}J_{HH}$ = 6.9 Hz, 6H, PCH(C*H*$_3)_2$), 1.24-1.09 (m, 18H, PCH(C*H*$_3)_2$).

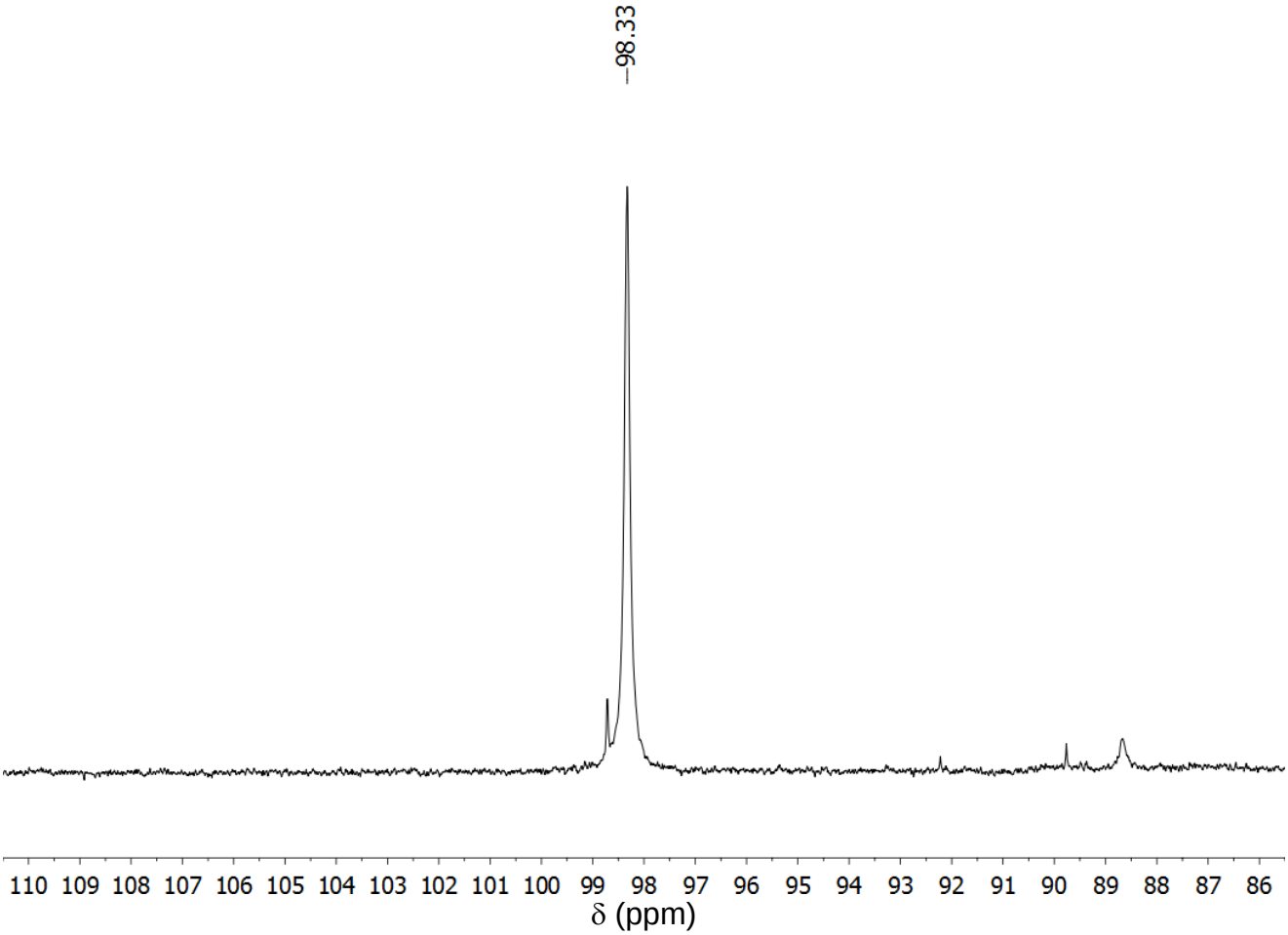


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of complex **8** in CD_2Cl_2 at 20°C. Residual impurities are also observed in this spectrum.

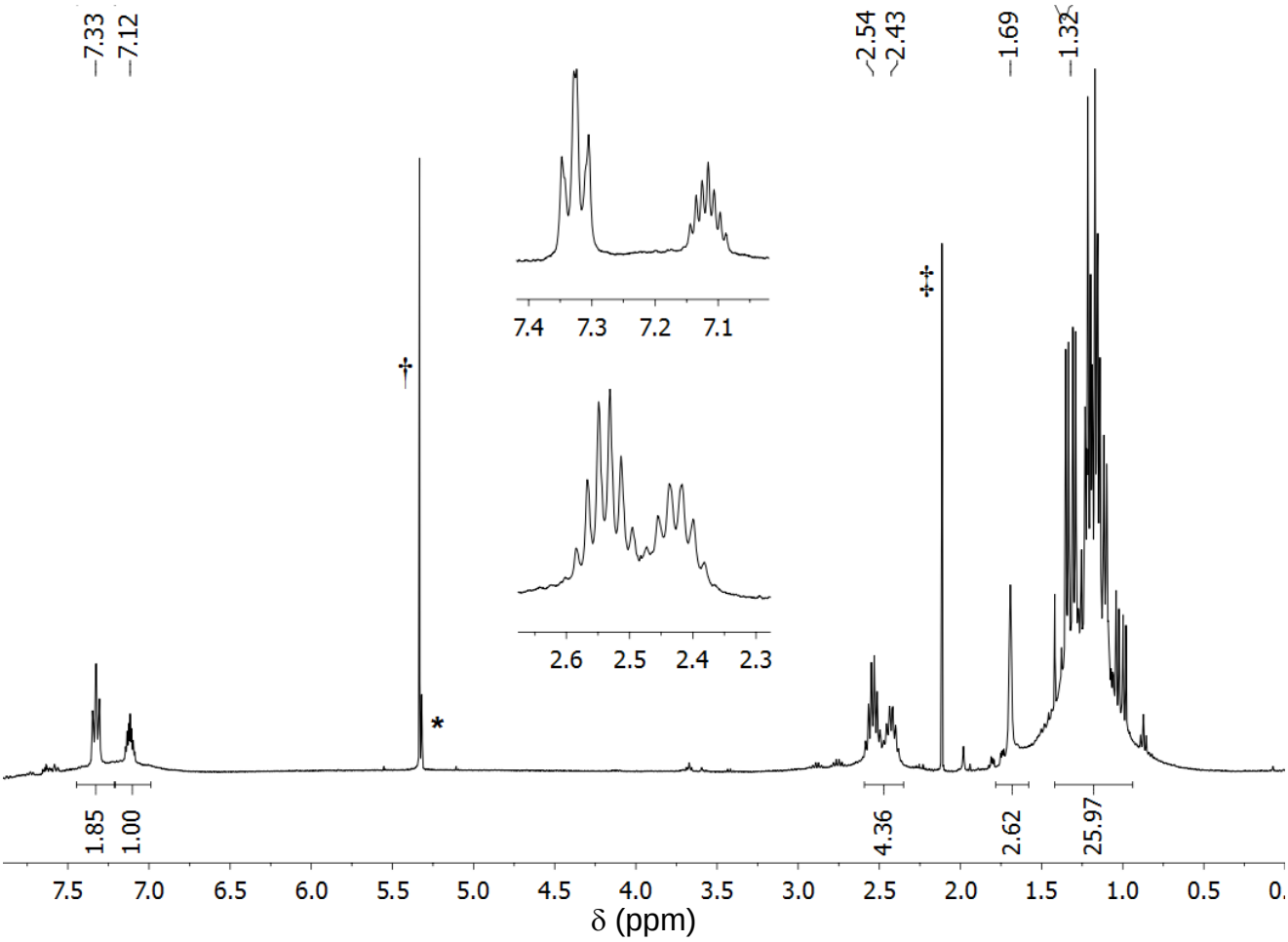


Figure S10. ^{1}H NMR spectrum of complex **8** in CD_2Cl_2 at 20°C. In addition to **8**, the following signals also appear in the spectrum: $CHDCl_2$ from the solvent (*), residual CH_2Cl_2 (†), and residual CH_3CN (‡).

Complex 9

$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_3OD, -70°C): 81.36 (s). ^{1}H NMR (500 MHz, CD_3OD, -70°C): 7.57 (m, $^{3}J_{HH}$ = 7.8 Hz, 2H, Ar–H), 7.30 (m, $^{3}J_{HH}$ = 7.7 Hz, 1H, Ar–H), 2.86 (m, $^{2}J_{PH} = {}^{3}J_{HH}$ = 6.7 Hz, 2H, PC*H*$(CH_3)_2$), 2.73 (m, $^{2}J_{PH} = {}^{3}J_{HH}$ = 7.2 Hz, 2H, PC*H*$(CH_3)_2$), 1.35-1.21 (m, 18H, PCH(C*H*$_3)_2$), 1.26 (d, $^{2}J_{RhH}$ = 1.3 Hz, 3H, Rh–C*H*$_3$), 1.14 (dd, $^{3}J_{PH}$ = 18.4 Hz, $^{3}J_{HH}$ = 6.9 Hz, 6H, PCH(C*H*$_3)_2$).

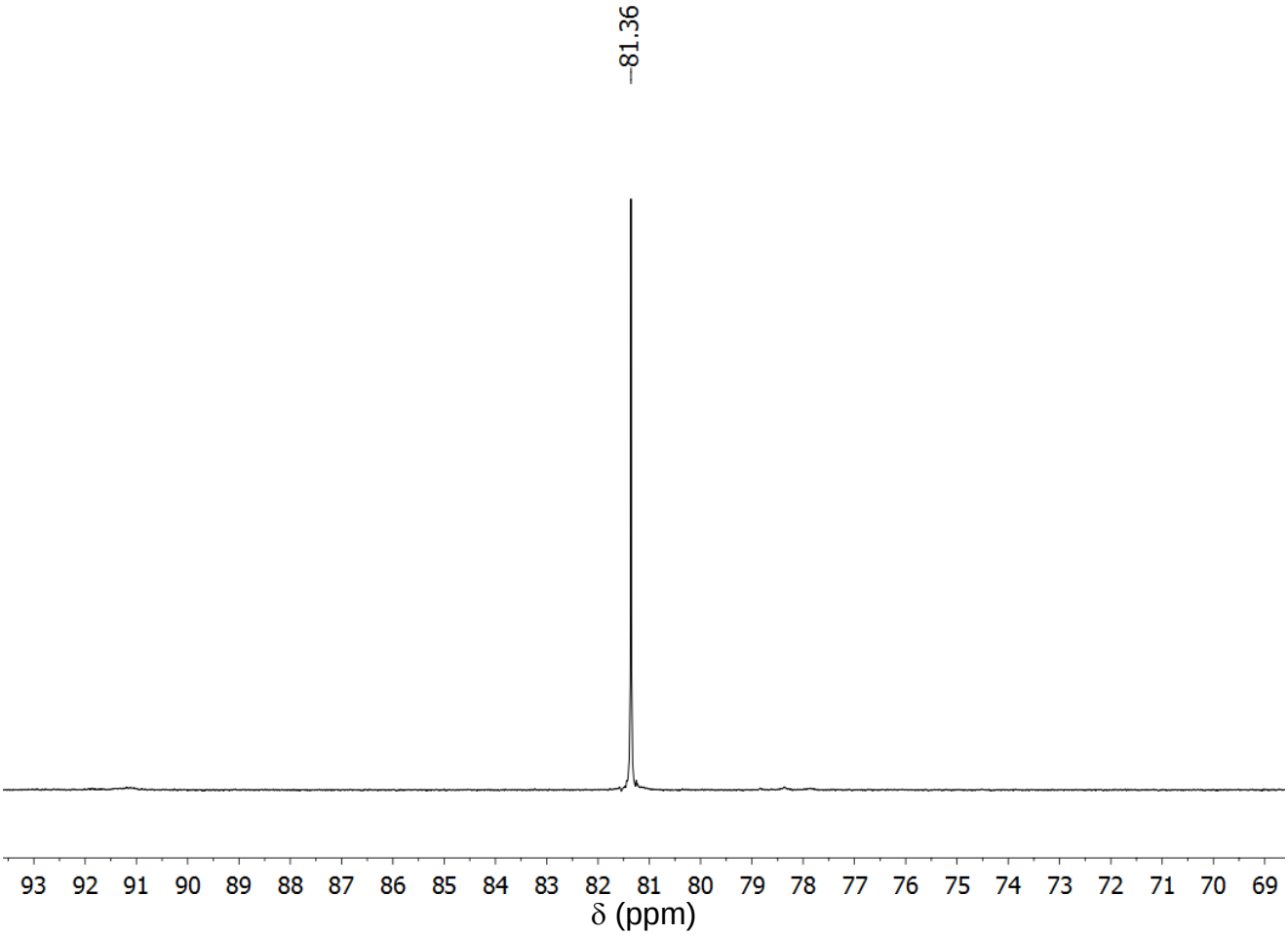


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of complex **9** in CH_3OD at -70°C.

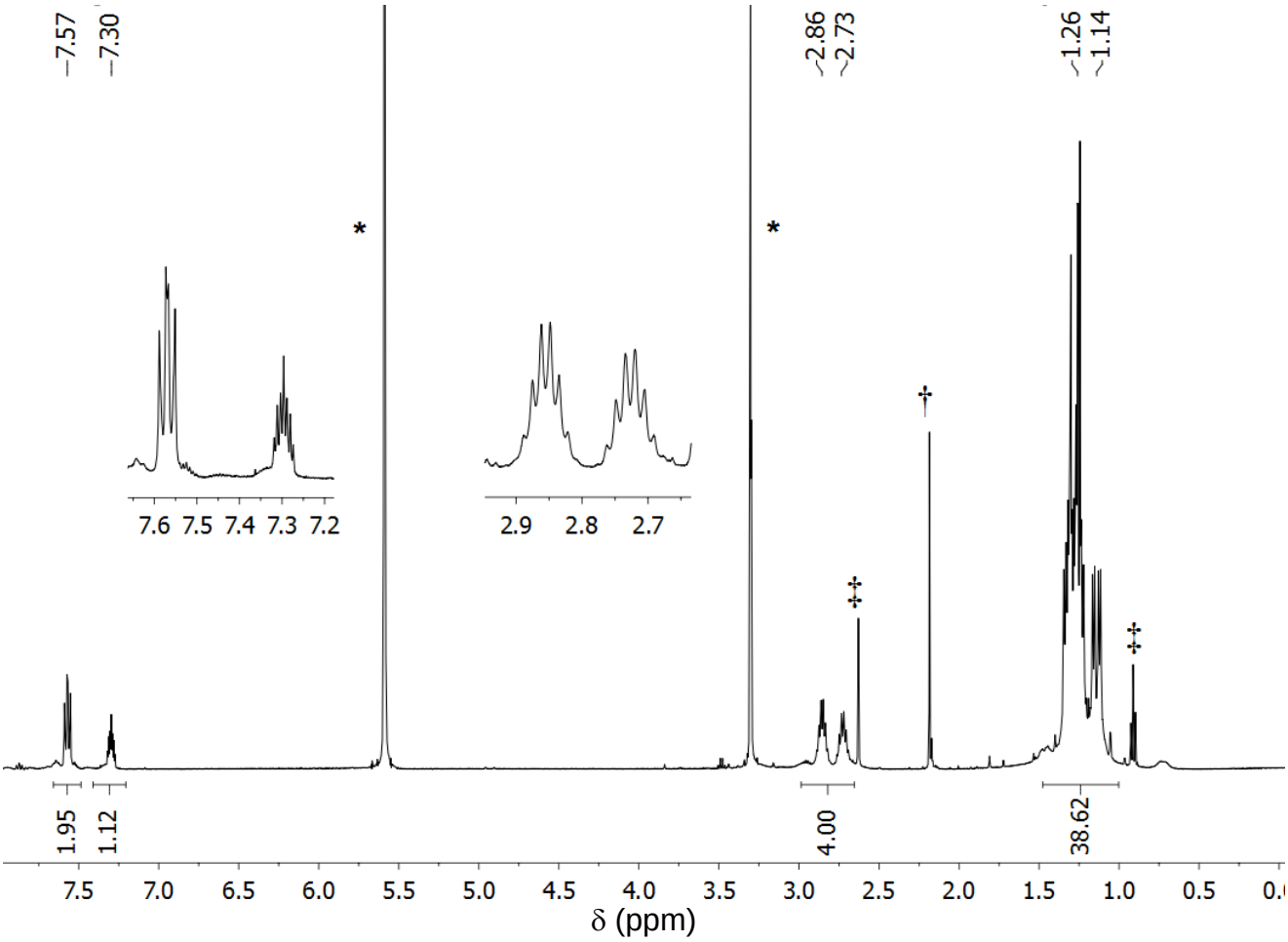


Figure S12. ^{1}H NMR spectrum of complex **9** in CH_3OD at -70°C. In addition to **9**, the following signals also appear in the spectrum: residual signals from the deuterated solvent (*), acetone from complex **2** used to prepare **9** (†), and unidentified impurities (‡).

Complex 10

$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_3OD, -40°C): 100.08 (s). ^{1}H NMR (500 MHz, CD_3OD, -40°C): 7.81 (m, $^{3}J_{HH}$ = 7.9 Hz, 2H, Ar–H), 7.44 (m, $^{3}J_{HH}$ = 7.7 Hz, 1H, Ar–H), 2.85 (m, $^{2}J_{PH} = {}^{3}J_{HH}$ = 7.1 Hz, 2H, PC*H*$(CH_3)_2$), 2.70 (m, $^{2}J_{PH} = {}^{3}J_{HH}$ = 7.2 Hz, 2H, PC*H*$(CH_3)_2$), 1.31 (dd, $^{3}J_{PH}$ = 17.7 Hz, $^{3}J_{HH}$ = 7.1 Hz, 6H, PCH(C*H*$_3)_2$), 1.30 (dd, $^{3}J_{PH}$ = 17.9 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, PCH(C*H*$_3)_2$), 1.20 (dd, $^{3}J_{PH}$ = 18.0 Hz, $^{3}J_{HH}$ = 6.7 Hz, 6H, PCH(C*H*$_3)_2$), 1.18 (dd, $^{3}J_{PH}$ = 18.3 Hz, $^{3}J_{HH}$ = 6.6 Hz, 6H, PCH(C*H*$_3)_2$), 0.99 (d, $^{2}J_{RhH}$ = 2.2 Hz, 3H, Rh–C*H*$_3$).

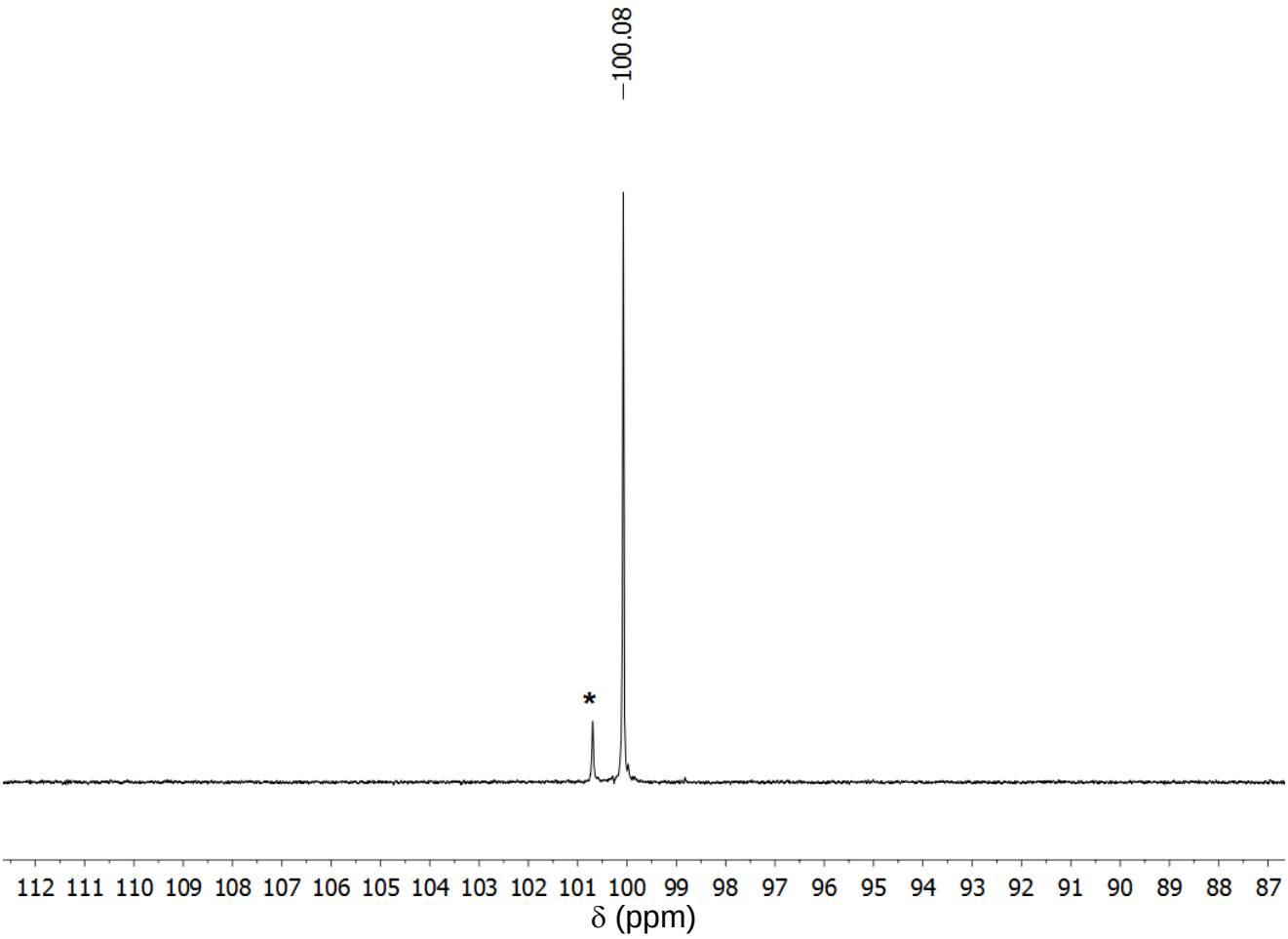


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of complex **10** in CH_3OD at -40°C. An unidentified impurity also appears in the spectrum (*).

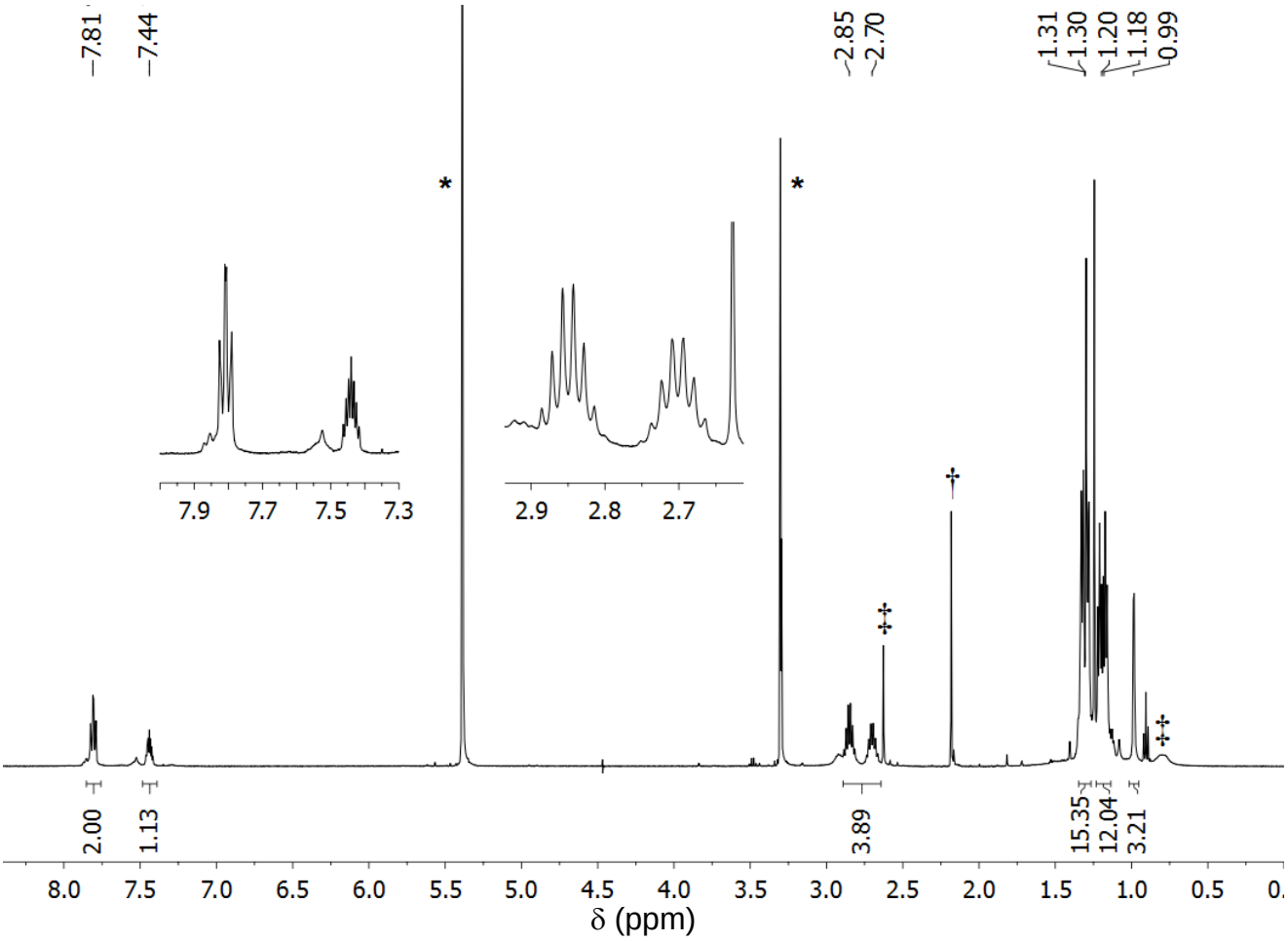


Figure S14. ^{1}H NMR spectrum of complex **10** in CH_3OD at -40°C. In addition to **10**, the following signals also appear in the spectrum: residual signals from the deuterated solvent (*), acetone from complex **2** used to prepare **10** (†), and unidentified impurities (‡).

Part II: Computed atomic properties for SCS and PCP complexes

Table S1. Atomic properties for selected atoms of the PCP and SCS complexes

Net atomic charges q(A)

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	0.19	0.36	0.40	0.45	0.32	0.42	0.39	0.33	0.53	0.59	0.60	0.48	0.56
C_{ipso}	-0.13	-0.15	-0.24	-0.13	-0.08	-0.08	0.03	-0.03	-0.07	-0.15	-0.04	-0.04	-0.19
C_{ortho}	-0.02	-0.02	-0.02	-0.01	-0.65	-0.66	-0.65	-0.64	-0.69	-0.70	-0.68	-0.68	-0.70
C_{meta}	-0.02	-0.03	-0.01	-0.03	0.01	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
C_{para}	0.00	-0.02	0.01	-0.02	0.02	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.00
H_{phenyl}	0.05	0.03	0.03	0.04	0.08	0.07	0.06	0.08	0.06	0.03	0.03	0.06	0.06
H_{phenyl}	0.05	0.03	0.03	0.04	0.08	0.07	0.07	0.08	0.07	0.06	0.06	0.06	0.07
H_{phenyl}	0.06	0.04	0.04	0.04	0.09	0.08	0.07	0.08	0.06	0.03	0.03	0.07	0.06
P/S	1.80	1.81	1.85	1.87	-0.78	-0.79	-0.73	-0.76	-0.81	-0.69	-0.72	-0.77	-0.75
C_{CH_3}	0.00	-0.05	-0.04	-0.16	0.02	0.05	0.05	-0.03	-0.05	-0.04	-0.12	-0.15	-0.16
H_{CH_3}	0.05	0.00	0.01	-0.02	0.03	0.01	0.01	0.07	0.01	0.00	0.00	0.05	0.06
H_{CH_3}	0.05	0.01	0.04	-0.01	0.06	0.03	0.04	0.07	0.01	0.03	-0.03	0.05	0.05
H_{CH_3}	0.00	0.00	0.01	-0.04	0.03	0.03	0.01	0.01	0.01	0.03	0.00	0.05	0.04
C_{CO}	1.06		1.09	1.12	1.11	1.09	1.08	1.11		1.15	1.14	1.12	1.19
O_{CO}	-1.22		-1.17	-1.18	-1.21	-1.21	-1.22	-1.20		-1.15	-1.17	-1.19	-1.19

Lagrangian of Atom A L(A) = -¼ Atomic Integral of the Laplacian of the Electron Density

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	0.00	40.69	40.43	40.43	40.74	40.65	40.68	40.72	40.69	40.42	40.46	0.00	0.00
C_{ipso}	0.00	37.90	37.91	37.90	37.90	37.89	37.86	37.87	37.86	37.87	37.84	0.00	0.00
C_{ortho}	0.00	37.90	37.90	37.91	38.18	38.19	38.17	38.17	38.22	38.22	38.21	0.00	0.00
C_{meta}	0.00	37.90	37.89	37.90	37.89	37.90	37.90	37.89	37.89	37.88	37.88	0.00	0.00
C_{para}	0.00	37.89	37.88	37.90	37.89	37.90	37.89	37.89	37.89	37.88	37.89	0.00	0.00
H_{phenyl}	0.00	0.59	0.60	0.59	0.58	0.58	0.59	0.58	0.58	0.60	0.60	0.00	0.00
H_{phenyl}	0.00	0.59	0.60	0.59	0.58	0.58	0.59	0.58	0.58	0.59	0.58	0.00	0.00
H_{phenyl}	0.00	0.59	0.59	0.59	0.57	0.58	0.58	0.57	0.58	0.60	0.60	0.00	0.00
P/S	0.00	340.4	340.4	340.3	398.2	398.2	398.1	398.1	398.2	398.1	398.2	0.00	0.00
C_{CH_3}	0.00	37.76	37.74	37.78	37.80	37.79	37.81	37.82	37.77	37.75	37.79	0.00	0.00
H_{CH_3}	0.00	0.61	0.61	0.60	0.60	0.61	0.61	0.58	0.60	0.61	0.60	0.00	0.00
H_{CH_3}	0.00	0.59	0.59	0.61	0.58	0.59	0.59	0.58	0.60	0.59	0.62	0.00	0.00
H_{CH_3}	0.00	0.61	0.61	0.62	0.60	0.60	0.61	0.61	0.59	0.59	0.60	0.00	0.00
C_{CO}	0.00		37.09	37.09	37.12	37.11	37.17	37.12		37.09	37.07	0.00	0.00
O_{CO}	0.00		75.82	75.84	75.82	75.83	75.81	75.82		75.83	75.84	0.00	0.00

Percentage of average number of electrons in atom A that are localized in atom A

%Loc(A) = 100 * LI(A) / N(A)

	PCP complexes				SCS complexes								
%Loc(A)	**23**	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	85.89	85.96	83.56	83.78	87.01	85.74	86.85	86.81	86.36	84.28	84.50	84.88	84.15
C_{ipso}	64.65	65.19	66.06	65.01	64.48	64.37	64.25	64.21	64.81	66.19	64.60	64.10	66.35
C_{ortho}	64.59	64.77	64.76	64.73	68.18	68.21	68.29	68.23	68.50	68.43	68.44	68.37	68.42
C_{meta}	65.79	65.82	65.76	65.81	65.70	65.59	65.63	65.70	65.68	65.59	65.58	65.63	65.71
C_{para}	65.82	65.83	65.75	65.84	65.89	65.85	65.87	65.91	65.92	65.82	65.83	65.94	65.91
H_{phenyl}	42.26	42.93	43.33	42.89	40.47	40.86	40.93	40.66	41.72	42.91	42.72	41.70	41.77
H_{phenyl}	42.27	42.93	43.33	42.86	40.46	40.83	41.00	40.67	41.79	42.43	42.36	41.70	41.87
H_{phenyl}	42.38	43.01	43.01	43.03	41.23	41.68	41.88	41.37	41.72	42.91	42.78	41.82	41.76
P/S	86.04	86.25	86.04	86.08	92.26	92.28	92.27	92.34	92.54	92.17	92.30	92.39	92.29
C_{CH_3}	65.94	66.19	66.28	66.72	66.00	65.94	65.86	65.95	66.19	66.28	66.47	66.41	66.90
H_{CH_3}	41.56	43.23	42.97	43.90	41.08	41.61	41.23	40.43	42.84	42.89	42.91	40.92	40.29
H_{CH_3}	41.56	43.34	41.68	42.97	41.57	43.11	42.61	40.43	42.86	42.28	43.46	40.93	41.85
H_{CH_3}	40.31	43.23	42.97	43.53	40.69	41.55	41.76	38.73	43.32	42.28	43.60	39.46	41.85
C_{CO}	67.54		70.37	70.58	67.64	68.51	67.31	67.77		70.53	71.73	69.51	65.20
O_{CO}	90.21		90.07	90.10	90.22	90.23	90.21	90.22		90.09	90.11	90.21	89.96

Magnitudes of intra-atomic dipole moments $|\mu_{intra}(A)|$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	0.34	0.05	0.09	0.12	0.29	0.40	0.40	0.34	0.16	0.11	0.19	0.26	0.26
C_{ipso}	0.13	0.25	0.47	0.19	0.18	0.26	0.09	0.09	0.29	0.55	0.25	0.21	0.56
C_{ortho}	0.09	0.06	0.07	0.06	1.03	1.04	1.02	1.03	1.04	1.03	1.05	1.05	1.03
C_{meta}	0.13	0.12	0.11	0.12	0.15	0.15	0.14	0.14	0.12	0.09	0.10	0.13	0.12
C_{para}	0.13	0.12	0.12	0.13	0.17	0.17	0.17	0.17	0.17	0.15	0.15	0.17	0.16
H_{phenyl}	0.13	0.13	0.13	0.13	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
H_{phenyl}	0.13	0.13	0.13	0.13	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
H_{phenyl}	0.13	0.13	0.12	0.13	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
P/S	1.44	1.49	1.41	1.41	0.57	0.60	0.40	0.48	0.54	0.49	0.58	0.52	0.53
C_{CH_3}	0.08	0.12	0.08	0.31	0.11	0.11	0.09	0.06	0.08	0.06	0.24	0.11	0.14
H_{CH_3}	0.13	0.14	0.13	0.14	0.12	0.13	0.12	0.12	0.14	0.14	0.15	0.14	0.14
H_{CH_3}	0.13	0.14	0.14	0.14	0.13	0.13	0.13	0.12	0.14	0.14	0.14	0.14	0.14
H_{CH_3}	0.11	0.14	0.13	0.13	0.13	0.11	0.11	0.09	0.14	0.14	0.14	0.14	0.14
C_{CO}	1.27		1.41	1.41	1.27	1.31	1.25	1.27		1.39	1.44	1.36	1.12
O_{CO}	0.77		0.87	0.85	0.79	0.79	0.76	0.79		0.89	0.89	0.83	0.75

Magnitudes of bonding dipole moment contributions |Mu_Bond(A)|

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	0.14	0.76	0.49	0.67	0.25	0.25	0.35	0.20	0.31	0.36	0.46	0.15	0.07
C_{ipso}	0.30	0.73	0.70	0.53	0.05	0.09	0.21	0.04	0.25	0.39	0.22	0.11	0.24
C_{ortho}	0.06	0.19	0.11	0.15	1.36	1.36	1.20	1.32	1.45	1.54	1.44	1.47	1.58
C_{meta}	0.04	0.10	0.04	0.09	0.12	0.11	0.11	0.12	0.06	0.01	0.03	0.06	0.07
C_{para}	0.06	0.01	0.03	0.01	0.13	0.11	0.10	0.11	0.08	0.06	0.07	0.08	0.08
H_{phenyl}	0.03	0.02	0.01	0.02	0.04	0.04	0.03	0.04	0.03	0.01	0.01	0.03	0.03
H_{phenyl}	0.03	0.02	0.01	0.02	0.05	0.04	0.04	0.04	0.04	0.03	0.03	0.03	0.04
H_{phenyl}	0.03	0.02	0.02	0.02	0.05	0.05	0.04	0.05	0.03	0.01	0.01	0.04	0.03
P/S	0.62	0.65	0.64	0.50	1.72	1.76	1.41	1.61	1.69	1.40	1.57	1.63	1.59
C_{CH_3}	0.14	0.25	0.14	0.65	0.07	0.03	0.16	0.09	0.23	0.15	0.45	0.14	0.17
H_{CH_3}	0.03	0.01	0.00	0.02	0.04	0.04	0.01	0.03	0.01	0.01	0.01	0.03	0.04
H_{CH_3}	0.03	0.00	0.02	0.03	0.03	0.01	0.03	0.06	0.01	0.01	0.02	0.03	0.02
H_{CH_3}	0.11	0.01	0.00	0.04	0.03	0.06	0.02	0.01	0.00	0.01	0.01	0.03	0.02
C_{CO}	1.18		1.05	1.04	1.09	1.12	1.16	1.08		0.91	0.93	1.04	0.94
O_{CO}	1.78		1.70	1.72	1.76	1.76	1.78	1.75		1.66	1.68	1.73	1.74

Average number of electron pairs formed in atom A D2(A,A) = (1/2)[N(A) * N(A) - LI(A)]

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	134.0	131.2	130.9	130.0	131.8	130.4	130.7	131.7	128.5	127.8	127.6	129.4	128.2
C_{ipso}	16.78	16.91	17.42	16.81	16.51	16.51	15.92	16.25	16.44	16.89	16.30	16.29	17.08
C_{ortho}	16.17	16.17	16.15	16.12	19.83	19.92	19.87	19.79	20.11	20.15	20.04	20.03	20.14
C_{meta}	16.14	16.19	16.08	16.17	16.00	16.03	16.04	16.00	16.04	16.01	15.97	16.02	16.05
C_{para}	16.05	16.14	15.98	16.15	15.94	15.98	16.01	15.98	16.02	15.95	15.94	16.05	16.02
H_{phenyl}	0.25	0.26	0.26	0.26	0.24	0.24	0.25	0.24	0.25	0.26	0.26	0.25	0.25
H_{phenyl}	0.25	0.26	0.26	0.26	0.24	0.24	0.25	0.24	0.24	0.24	0.24	0.25	0.24
H_{phenyl}	0.24	0.26	0.25	0.26	0.23	0.23	0.24	0.23	0.25	0.26	0.26	0.24	0.25
P/S	81.5	81.3	80.8	80.6	133.1	133.2	132.3	132.7	133.6	131.6	132.1	132.9	132.6
C_{CH_3}	16.04	16.32	16.23	16.94	15.93	15.72	15.76	16.22	16.27	16.24	16.71	16.87	16.93
H_{CH_3}	0.25	0.28	0.28	0.29	0.27	0.28	0.28	0.25	0.28	0.28	0.28	0.26	0.25
H_{CH_3}	0.25	0.28	0.26	0.30	0.25	0.26	0.26	0.25	0.28	0.27	0.31	0.26	0.26
H_{CH_3}	0.30	0.28	0.28	0.31	0.28	0.27	0.28	0.30	0.27	0.27	0.28	0.26	0.26
C_{CO}	10.51		10.32	10.21	10.31	10.36	10.45	10.30		10.05	10.06	10.20	10.02
O_{CO}	38.33		37.91	38.04	38.21	38.27	38.33	38.19		37.74	37.88	38.07	38.06

D2(A,Mol) = D2(A,A) + D2(A,A'), where D2(A,A') = (1/2)[N(A) * N(A') - DI(A,A') / 2] is half of average number of electron pairs formed between atom a and other atoms of molecule

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	1336.1	1206.	1319.7	1315.4	1459.4	1600.4	1602.8	1458.8	1325.7	1436.2	1435.3	1445.1	1438.5
C_{ipso}	487.0	445.9	496.2	487.5	531.7	586.5	576.5	527.7	488.4	538.3	528.6	528.3	541.2
C_{ortho}	478.4	436.4	478.4	477.9	581.6	642.9	642.2	581.2	538.9	586.2	584.6	584.6	586.1
C_{meta}	478.6	437.1	477.8	479.0	524.5	578.9	579.2	524.5	483.2	524.6	524.1	524.8	525.3
C_{para}	477.4	436.5	476.4	478.7	523.7	578.2	578.8	524.3	483.0	523.9	523.8	525.4	524.9
H_{phenyl}	75.49	70.01	77.42	76.62	80.56	89.88	90.28	80.90	75.63	84.98	84.63	82.19	82.31
H_{phenyl}	75.49	70.01	77.42	76.58	80.68	89.96	90.20	80.91	74.67	82.49	82.40	82.19	81.33
H_{phenyl}	74.84	69.66	76.10	76.51	79.63	89.13	89.77	80.10	75.63	84.98	84.71	81.38	82.31
P/S	1049.	956.2	1045.	1044.	1468.	1620.	1615.	1466.	1354.	1460.	1463.	1468.	1466.
C_{CH_3}	477.2	438.9	480.1	490.0	523.6	573.9	574.5	528.0	486.7	528.6	535.8	538.1	539.3
H_{CH_3}	75.50	72.43	79.00	80.73	84.70	95.27	95.20	81.59	79.98	87.29	87.43	83.08	81.85
H_{CH_3}	75.51	71.74	76.55	80.59	82.49	93.78	92.68	81.55	80.02	85.20	90.16	83.12	83.56
H_{CH_3}	79.44	72.43	79.00	82.29	85.17	93.81	95.58	86.44	79.47	85.20	87.78	83.23	83.56
C_{CO}	392.4		390.3	388.3	428.0	473.5	474.8	427.9		424.3	425.1	426.8	421.2
O_{CO}	732.8		729.0	730.2	805.4	888.9	889.5	805.2		800.6	802.0	804.0	803.7

Electron localization index LI(A) = average number of electrons localized in atom A

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	14.43	14.30	13.87	13.86	14.51	14.22	14.43	14.47	14.22	13.83	13.86	14.02	13.83
C_{ipso}	3.96	4.01	4.12	3.99	3.92	3.91	3.84	3.87	3.93	4.07	3.90	3.87	4.10
C_{ortho}	3.89	3.90	3.90	3.89	4.53	4.54	4.54	4.53	4.59	4.59	4.57	4.57	4.58
C_{meta}	3.96	3.97	3.95	3.96	3.94	3.93	3.94	3.94	3.94	3.93	3.93	3.94	3.94
C_{para}	3.95	3.96	3.94	3.96	3.94	3.95	3.95	3.95	3.96	3.94	3.94	3.96	3.95
H_{phenyl}	0.40	0.41	0.42	0.41	0.37	0.38	0.38	0.38	0.39	0.42	0.41	0.39	0.39
H_{phenyl}	0.40	0.41	0.42	0.41	0.37	0.38	0.38	0.38	0.39	0.40	0.40	0.39	0.39
H_{phenyl}	0.40	0.41	0.41	0.41	0.38	0.38	0.39	0.38	0.39	0.42	0.41	0.39	0.39
P/S	11.36	11.37	11.32	11.31	15.49	15.49	15.44	15.48	15.56	15.38	15.44	15.50	15.46
C_{CH_3}	3.96	4.01	4.00	4.11	3.95	3.92	3.92	3.98	4.00	4.00	4.07	4.08	4.12
H_{CH_3}	0.39	0.43	0.43	0.45	0.40	0.41	0.41	0.38	0.43	0.43	0.43	0.39	0.38
H_{CH_3}	0.39	0.43	0.40	0.44	0.39	0.42	0.41	0.38	0.43	0.41	0.45	0.39	0.40
H_{CH_3}	0.40	0.43	0.43	0.45	0.40	0.40	0.41	0.38	0.43	0.41	0.44	0.38	0.40
C_{CO}	3.33		3.45	3.45	3.31	3.36	3.31	3.31		3.42	3.49	3.39	3.14
O_{CO}	8.32		8.26	8.27	8.31	8.31	8.32	8.30		8.24	8.26	8.29	8.26

Average number of electrons in Vol(A)=0.001 au N(Vol(A)),0.001

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	44.79	44.62	44.59	44.53	44.66	44.58	44.59	44.65	44.45	44.40	44.39	44.50	44.43
C_{ipso}	6.12	6.14	6.24	6.13	6.07	6.08	5.97	6.03	6.06	6.15	6.04	6.04	6.18
C_{ortho}	6.01	6.01	6.01	6.00	6.64	6.65	6.65	6.63	6.69	6.69	6.67	6.68	6.69
C_{meta}	6.01	6.01	5.99	6.01	5.98	5.99	5.99	5.98	5.99	5.98	5.98	5.98	5.99
C_{para}	5.99	6.00	5.97	6.00	5.97	5.97	5.98	5.97	5.98	5.97	5.97	5.98	5.98
H_{phenyl}	0.93	0.95	0.95	0.94	0.91	0.92	0.92	0.91	0.92	0.96	0.95	0.92	0.93
H_{phenyl}	0.93	0.95	0.95	0.94	0.91	0.92	0.92	0.91	0.91	0.92	0.92	0.92	0.91
H_{phenyl}	0.92	0.94	0.94	0.94	0.89	0.90	0.91	0.90	0.92	0.96	0.95	0.91	0.93
P/S	13.20	13.19	13.15	13.13	16.73	16.74	16.69	16.70	16.76	16.64	16.67	16.72	16.70
C_{CH_3}	6.00	6.05	6.03	6.16	5.98	5.94	5.95	6.03	6.04	6.03	6.11	6.14	6.15
H_{CH_3}	0.93	0.98	0.98	0.99	0.96	0.98	0.98	0.92	0.98	0.98	0.98	0.94	0.92
H_{CH_3}	0.93	0.97	0.95	1.00	0.93	0.95	0.94	0.92	0.98	0.96	1.02	0.94	0.94
H_{CH_3}	0.99	0.98	0.98	1.02	0.96	0.96	0.98	0.98	0.97	0.96	0.98	0.94	0.94
C_{CO}	4.93		4.90	4.88	4.88	4.90	4.91	4.88		4.84	4.85	4.87	4.81
O_{CO}	9.17		9.13	9.15	9.16	9.17	9.18	9.16		9.11	9.13	9.15	9.15

Traceless form of quadrupole moment tensor of atom A's electronic charge density distribution, using the nucleus of atom A as origin Q(A)

$$Q_{xx}^{A} = -[3\langle\rho_{x^2}\rangle^{A} - \langle\rho_{r^2}\rangle^{A}]$$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	2.15	0.96	-0.08	-0.37	2.52	1.00	2.42	2.70	1.44	0.65	0.22	1.28	0.78
C_{ipso}	1.46	2.00	2.20	1.50	1.34	1.09	1.27	1.31	1.71	1.96	1.56	1.17	2.24
C_{ortho}	1.30	1.55	1.54	1.20	0.00	-0.40	-0.02	0.09	0.13	0.04	0.03	0.07	0.09
C_{meta}	1.57	1.67	1.61	1.30	1.27	1.24	1.33	1.30	1.36	1.45	1.42	1.33	1.38
C_{para}	1.82	1.92	1.81	1.61	1.82	1.65	1.90	1.90	1.95	1.89	1.92	1.99	1.93
H_{phenyl}	0.29	0.30	0.30	0.26	0.33	0.31	0.31	0.31	0.29	0.31	0.30	0.29	0.30
H_{phenyl}	0.29	0.30	0.30	0.27	0.30	0.30	0.33	0.31	-0.17	-0.17	-0.17	0.29	-0.17
H_{phenyl}	-0.16	-0.17	-0.17	-0.17	-0.16	-0.17	-0.16	-0.16	0.29	0.31	0.31	-0.17	0.30
P/S	-2.06	-2.09	-1.93	-1.88	1.37	0.99	1.09	1.73	1.90	1.66	1.74	1.97	1.95
C_{CH_3}	-0.23	0.11	0.05	0.38	-0.22	-0.23	-0.15	-0.30	0.14	-0.01	0.40	0.11	0.17
H_{CH_3}	0.27	0.29	0.29	-0.15	0.42	0.20	0.19	0.27	0.27	-0.23	0.12	0.24	-0.22
H_{CH_3}	0.27	-0.22	-0.24	0.17	-0.02	-0.21	-0.21	0.27	0.27	0.25	0.44	0.24	0.23
H_{CH_3}	-0.35	0.29	0.29	0.43	-0.09	0.31	0.40	-0.30	-0.22	0.24	-0.20	-0.21	0.23
C_{CO}	-0.97		-1.06	-0.87	-0.78	-0.79	-0.80	-0.79		-0.77	-0.57	-0.64	-1.25
O_{CO}	-0.07		-0.01	0.03	-0.04	-0.05	-0.09	-0.04		0.03	0.04	0.00	-0.10

$$Q_{xy}^{A} = -3\langle\rho_{xy}\rangle^{A}$$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	0.00	0.00	0.01	0.02	-0.54	-1.33	-0.61	-0.01	0.02	0.00	-0.02	-0.01	-0.03
C_{ipso}	0.00	0.00	0.00	0.09	-0.13	-0.67	0.12	0.00	0.00	0.00	-0.02	0.00	0.00
C_{ortho}	0.32	0.06	0.01	0.15	-0.93	-1.27	1.14	-1.03	1.72	1.65	-1.67	1.63	-1.67
C_{meta}	0.36	-0.21	-0.17	-0.12	0.25	-0.01	-0.33	0.39	-0.22	-0.16	0.17	-0.27	0.20
C_{para}	0.00	0.00	0.00	0.09	-0.19	-0.67	0.09	0.00	0.00	0.00	-0.01	0.00	0.00
H_{phenyl}	-0.14	0.25	0.25	0.25	-0.07	-0.16	0.14	-0.09	0.24	0.24	-0.25	0.22	-0.24
H_{phenyl}	0.14	-0.25	-0.25	-0.23	0.05	0.03	-0.10	0.09	0.00	0.00	0.01	-0.22	0.00
H_{phenyl}	0.00	0.00	0.00	0.00	-0.02	0.01	-0.02	0.00	-0.24	-0.24	0.23	0.00	0.24
P/S	-1.70	-1.94	-1.78	-2.00	1.13	0.63	-1.12	1.20	1.03	1.34	-1.03	-1.00	-1.54
C_{CH_3}	0.00	0.00	0.00	0.05	-0.07	-0.03	-0.03	0.00	0.00	0.00	0.04	0.00	0.00
H_{CH_3}	0.15	0.18	0.28	0.18	-0.02	-0.31	0.30	0.16	0.23	0.00	-0.29	-0.26	0.00
H_{CH_3}	-0.15	0.00	0.00	-0.32	-0.22	0.06	-0.06	-0.16	-0.23	0.26	0.25	0.26	-0.26
H_{CH_3}	0.00	-0.18	-0.28	0.12	0.22	0.31	-0.30	0.00	0.00	-0.26	0.10	0.00	0.26
C_{CO}	0.00		0.00	0.02	-0.29	-0.60	-0.56	0.00		0.00	0.10	0.00	0.00
O_{CO}	0.00		0.00	0.01	-0.02	-0.02	-0.04	0.00		0.00	-0.02	0.00	0.00

$$Q_{xz}^{A} = -3\langle\rho_{xz}\rangle^{A}$$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	0.00	-0.01	0.00	-0.29	-1.67	-1.94	0.06	0.00	-0.01	0.01	0.15	0.01	-0.01
C_{ipso}	0.00	0.00	0.00	-1.29	0.13	0.40	-0.01	0.00	0.00	0.00	0.06	0.00	0.00
C_{ortho}	0.41	-0.39	-0.39	-1.33	-1.57	-1.07	1.17	-1.39	0.13	0.06	-0.18	0.71	-0.18
C_{meta}	-0.01	-0.15	-0.16	-1.31	0.12	0.40	0.01	-0.01	0.00	0.02	0.08	0.13	-0.05
C_{para}	0.00	0.00	0.00	-1.35	0.15	0.73	-0.09	0.00	0.00	0.00	0.07	0.00	0.00
H_{phenyl}	0.20	0.00	0.01	-0.13	-0.20	-0.18	0.20	-0.21	0.00	-0.01	0.00	0.10	-0.01
H_{phenyl}	-0.20	0.00	-0.01	-0.16	0.24	0.26	-0.20	0.21	0.00	0.00	0.00	-0.10	0.00
H_{phenyl}	0.00	0.00	0.00	-0.03	-0.01	0.03	-0.02	0.00	0.00	0.01	0.05	0.00	0.01
P/S	0.07	-0.22	-0.45	0.35	-1.23	-1.66	0.93	-0.50	-0.67	-0.71	0.37	0.13	0.73
C_{CH_3}	0.00	0.00	0.00	-0.12	-0.04	-0.02	-0.05	0.00	0.00	0.00	0.00	0.00	0.00
H_{CH_3}	0.22	-0.23	0.11	0.04	-0.17	-0.05	-0.01	-0.25	0.22	0.00	0.16	0.13	0.00
H_{CH_3}	-0.22	0.00	0.00	0.15	0.18	-0.04	0.07	0.25	-0.22	-0.13	-0.09	-0.13	0.14
H_{CH_3}	0.00	0.23	-0.11	-0.17	0.07	0.11	-0.05	0.00	0.00	0.13	0.03	0.00	-0.14
C_{CO}	0.00		0.00	-0.14	-0.05	0.18	-0.49	0.00		0.00	-0.42	0.00	0.00
O_{CO}	0.00		0.00	0.00	0.00	0.02	-0.04	0.00		0.00	0.02	0.00	0.00

$$Q_{yy}^{A} = -[3<\rho_{y^2}>^{A} - <\rho_{r^2}>^{A}]$$

	PCP complexes				SCS complexes								
Q_YY(A)	**23**	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	2.38	0.30	2.01	-1.07	3.32	-0.10	-1.89	-0.32	0.27	1.76	-0.80	-0.35	2.23
C_{ipso}	-1.39	1.56	1.08	1.36	-1.87	-1.62	-0.98	-1.34	1.22	0.55	0.99	0.36	0.75
C_{ortho}	-0.59	1.74	1.71	1.72	-0.70	0.54	0.48	-0.38	2.42	2.52	2.45	1.88	2.42
C_{meta}	-0.97	1.87	1.81	1.84	-1.45	-0.35	-0.01	-0.88	1.71	1.72	1.64	1.34	1.73
C_{para}	-0.94	1.49	1.35	1.52	-1.48	-0.25	-0.05	-1.01	1.42	1.44	1.39	1.14	1.41
H_{phenyl}	-0.16	0.00	0.01	0.02	-0.20	-0.11	-0.12	-0.17	0.00	0.00	0.00	-0.03	0.00
H_{phenyl}	-0.16	0.00	0.01	-0.01	-0.21	-0.18	-0.13	-0.17	0.44	0.45	0.44	-0.03	0.44
H_{phenyl}	0.07	0.45	0.45	0.46	-0.02	0.15	0.21	0.06	0.00	0.00	-0.01	0.39	0.00
P/S	0.97	0.78	0.77	0.54	1.24	0.76	1.26	1.68	0.91	1.43	0.39	0.94	0.95
C_{CH_3}	-0.06	-0.12	0.06	0.16	-0.20	-0.15	0.02	0.01	-0.11	0.10	0.08	0.28	-0.42
H_{CH_3}	-0.22	-0.19	-0.09	0.34	-0.25	0.03	0.05	-0.21	-0.16	0.39	0.01	-0.08	-0.15
H_{CH_3}	-0.22	0.44	0.37	0.01	0.05	0.23	0.04	-0.20	-0.16	-0.08	-0.20	-0.08	-0.06
H_{CH_3}	0.37	-0.19	-0.09	-0.23	0.26	-0.07	-0.11	0.37	0.44	-0.08	0.33	0.29	-0.06
C_{CO}	1.92		2.03	-0.97	2.01	0.12	0.28	0.67		1.72	-0.91	-0.33	-0.05
O_{CO}	0.12		0.02	-0.01	0.10	0.00	0.07	0.04		-0.05	0.02	-0.01	-0.02

$$Q_{yz}^{A} = -3<\rho_{yz}>^{A}$$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	5.22	1.14	0.07	0.05	-3.94	-3.89	5.88	-6.42	-0.74	-0.13	-0.37	-4.22	-2.42
C_{ipso}	-1.81	-0.17	0.16	0.29	1.13	0.88	1.53	1.62	0.15	-0.11	0.54	0.99	0.23
C_{ortho}	-2.18	0.22	0.46	0.32	1.86	2.04	2.27	2.25	0.30	0.04	0.59	1.50	0.32
C_{meta}	-2.63	0.22	0.46	0.39	2.27	2.35	2.25	2.39	0.28	0.02	0.56	1.31	0.25
C_{para}	-2.25	0.27	0.48	0.31	2.09	2.09	2.17	2.29	0.26	-0.01	0.53	1.27	0.19
H_{phenyl}	-0.15	0.00	0.02	-0.05	0.12	0.15	0.15	0.14	0.02	0.01	0.04	0.08	0.02
H_{phenyl}	-0.15	0.00	0.02	0.08	0.13	0.12	0.12	0.14	0.04	0.00	0.08	0.08	0.03
H_{phenyl}	-0.36	0.04	0.07	0.05	0.33	0.35	0.34	0.35	0.02	0.01	0.03	0.19	0.02
P/S	0.08	-0.06	-0.13	0.17	0.47	0.31	-1.47	-0.02	0.89	0.84	1.44	0.80	1.36
C_{CH_3}	-0.24	-0.14	0.08	-0.22	0.20	0.17	0.34	0.40	0.14	0.06	-0.14	0.13	-0.30
H_{CH_3}	0.06	-0.11	0.09	0.18	0.00	0.02	-0.04	-0.07	0.11	0.18	-0.17	-0.08	-0.14
H_{CH_3}	0.06	-0.02	-0.19	-0.19	-0.22	-0.28	-0.30	-0.08	0.11	-0.08	-0.04	-0.08	-0.08
H_{CH_3}	0.19	-0.11	0.09	-0.04	0.02	0.06	0.03	-0.20	-0.02	-0.08	0.24	0.11	-0.08
C_{CO}	1.76		-0.38	-0.43	-1.37	-1.95	1.96	-2.11		0.17	-0.64	-1.73	-1.40
O_{CO}	0.10		-0.01	-0.01	-0.07	-0.09	0.13	-0.10		0.01	0.00	-0.03	-0.07

$$Q_{zz}^{A} = -[3<\rho_{z^2}>^{A} - <\rho_{r^2}>^{A}]$$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	-4.53	-1.26	-1.93	1.43	-5.84	-0.91	-0.53	-2.38	-1.71	-2.40	0.58	-0.93	-3.01
C_{ipso}	-0.06	-3.56	-3.28	-2.85	0.53	0.52	-0.29	0.03	-2.93	-2.51	-2.55	-1.52	-3.00
C_{ortho}	-0.71	-3.29	-3.25	-2.92	0.70	-0.14	-0.46	0.30	-2.56	-2.56	-2.48	-1.95	-2.51
C_{meta}	-0.60	-3.54	-3.42	-3.14	0.18	-0.89	-1.31	-0.41	-3.08	-3.16	-3.07	-2.67	-3.12
C_{para}	-0.88	-3.41	-3.16	-3.12	-0.34	-1.40	-1.85	-0.89	-3.37	-3.32	-3.31	-3.13	-3.34
H_{phenyl}	-0.13	-0.30	-0.30	-0.27	-0.13	-0.20	-0.20	-0.14	-0.29	-0.31	-0.31	-0.26	-0.30
H_{phenyl}	-0.13	-0.30	-0.30	-0.26	-0.08	-0.12	-0.20	-0.14	-0.27	-0.28	-0.27	-0.26	-0.27
H_{phenyl}	0.09	-0.29	-0.28	-0.28	0.18	0.01	-0.04	0.10	-0.29	-0.31	-0.30	-0.22	-0.30
P/S	1.09	1.32	1.15	1.35	-2.61	-1.75	-2.35	-3.41	-2.81	-3.09	-2.13	-2.91	-2.89
C_{CH_3}	0.29	0.01	-0.11	-0.54	0.42	0.38	0.13	0.29	-0.03	-0.09	-0.48	-0.39	0.25
H_{CH_3}	-0.05	-0.10	-0.20	-0.19	-0.17	-0.23	-0.24	-0.06	-0.11	-0.16	-0.13	-0.16	0.37
H_{CH_3}	-0.05	-0.23	-0.12	-0.18	-0.03	-0.02	0.17	-0.06	-0.11	-0.17	-0.24	-0.16	-0.17
H_{CH_3}	-0.03	-0.10	-0.20	-0.21	-0.18	-0.24	-0.29	-0.07	-0.22	-0.17	-0.13	-0.08	-0.17
C_{CO}	-0.95		-0.97	1.84	-1.22	0.68	0.52	0.12		-0.96	1.47	0.97	1.30
O_{CO}	-0.05		-0.01	-0.02	-0.05	0.04	0.02	0.01		0.02	-0.06	0.02	0.12

Area of interatomic surface of atom A whose electron density is greater than 0.002, Area_IAS(A),0.002

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	180.40	189.05	254.48	259.27	176.07	215.44	265.12	190.04	36.32	243.36	245.78	207.32	196.19
C_{ipso}	122.77	97.23	103.27	101.42	82.55	159.35	88.35	134.41	100.53	106.64	105.78	129.92	98.47
C_{ortho}	115.49	104.37	105.20	104.36	114.11	115.66	116.98	134.45	122.46	124.25	123.29	128.98	121.47
C_{meta}	101.82	97.93	97.25	97.44	93.70	96.97	96.09	112.51	107.20	107.91	108.01	108.26	105.81
C_{para}	91.06	92.26	91.19	92.23	89.56	90.49	93.27	89.93	90.55	90.64	90.68	90.85	90.61
H_{phenyl}	27.77	27.45	27.37	27.27	34.59	33.92	34.92	34.34	31.32	31.91	32.01	31.64	30.78
H_{phenyl}	27.77	27.45	27.37	27.29	NA	34.69	35.36	34.31	24.56	24.73	24.73	31.64	24.61
H_{phenyl}	24.79	25.23	24.94	25.31	24.16	24.46	24.65	24.32	31.32	31.90	32.18	24.65	30.78
P/S	184.77	185.49	191.61	202.03	92.45	116.17	101.45	87.92	NA	91.16	94.48	90.67	88.78
C_{CH_3}	104.91	158.43	167.10	152.47	73.61	122.31	58.15	125.51	27.22	159.30	154.82	175.26	143.02
H_{CH_3}	33.46	35.04	34.47	29.09	15.95	49.14	9.46	36.60	NA	34.40	33.13	34.32	29.02
H_{CH_3}	33.47	27.25	31.77	41.44	30.58	26.72	26.85	36.54	NA	31.01	41.39	34.34	29.02
H_{CH_3}	46.53	35.05	34.47	42.60	56.72	50.94	47.67	64.54	27.22	31.00	28.41	32.54	28.98
C_{CO}	82.02		79.83	95.43	80.28	82.53	93.95	79.00		78.54	82.21	79.30	94.96
O_{CO}	32.95		32.23	37.26	32.49	32.77	36.07	32.21		31.61	37.28	32.30	35.80

Area of atom A's part of IsoDensity Surface (IDS) with electron density greater than 0.002, Area_IDS(A),0.002

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	32.68	40.74	17.97	23.04	34.47	14.02	25.61	34.17	35.26	17.60	18.78	24.54	20.40
C_{ipso}	8.52	17.89	14.37	11.40	7.10	4.06	6.24	8.44	14.83	12.65	9.78	6.24	19.48
C_{ortho}	12.31	18.15	17.73	17.13	15.72	17.98	15.89	16.67	18.66	18.20	17.54	15.19	18.92
C_{meta}	26.64	29.75	29.46	30.03	26.61	24.28	23.46	26.86	26.87	26.75	26.62	25.92	27.20
C_{para}	30.78	31.15	30.72	31.38	31.22	30.77	30.02	31.74	32.18	31.93	32.15	32.63	31.96
H_{phenyl}	32.34	33.22	33.52	33.20	24.89	25.76	24.92	25.66	28.78	29.75	29.35	28.47	30.01
H_{phenyl}	32.28	33.25	33.28	33.18	24.84	25.13	25.34	25.41	34.30	34.76	34.65	28.94	34.49
H_{phenyl}	35.43	35.01	35.19	35.11	34.03	34.05	34.36	33.96	29.00	29.72	29.34	34.41	29.01
P/S	5.74	8.99	4.37	7.33	88.17	82.12	78.46	90.01	94.64	86.55	86.32	89.12	89.39
C_{CH_3}	13.44	16.67	15.56	13.45	11.72	11.51	10.70	11.75	16.51	14.32	14.49	13.00	15.64
H_{CH_3}	26.93	28.15	27.41	34.08	17.97	16.38	14.33	21.84	27.84	28.59	29.51	25.27	29.80
H_{CH_3}	26.90	34.85	28.97	23.95	28.87	34.51	33.96	21.92	27.94	30.02	22.38	24.97	30.96
H_{CH_3}	20.48	27.87	27.33	21.67	18.38	16.77	14.17	15.61	34.37	30.00	33.94	25.43	31.27
C_{CO}	25.85		25.53	16.70	24.02	24.50	14.53	25.46		22.02	21.96	25.67	11.92
O_{CO}	90.38		89.67	86.26	90.34	90.08	88.01	90.08		89.71	86.48	89.79	85.24

Atomic Surface Area, Area(A),0.002 = Area_IAS(A|Total) + Area_IDS(A)

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	213.09	229.79	272.45	282.31	210.54	229.47	290.72	224.21	NA	260.96	264.55	231.86	216.59
C_{ipso}	131.29	115.12	117.64	112.82	NA	163.41	NA	142.85	115.36	119.29	115.56	136.16	117.96
C_{ortho}	127.79	122.53	122.93	121.49	129.83	133.65	132.87	151.12	141.12	142.45	140.83	144.18	140.40
C_{meta}	128.47	127.68	126.71	127.47	120.31	121.24	119.55	139.38	134.07	134.66	134.63	134.18	133.01
C_{para}	121.83	123.42	121.91	123.61	120.77	121.26	123.29	121.67	122.73	122.57	122.83	123.48	122.57
H_{phenyl}	60.11	60.67	60.89	60.47	59.48	59.68	59.85	60.00	60.10	61.65	61.36	60.11	60.78
H_{phenyl}	60.06	60.70	60.65	60.47	NA	59.82	60.70	59.71	58.86	59.49	59.37	60.57	59.10
H_{phenyl}	60.21	60.24	60.13	60.43	58.19	58.51	59.01	58.28	60.32	61.63	61.52	59.06	59.79
P/S	190.51	194.47	195.98	209.36	180.62	198.30	179.91	177.93	NA	177.71	180.81	179.79	178.17
C_{CH_3}	118.35	175.10	182.67	165.92	NA	133.82	NA	137.25	NA	173.62	169.30	188.27	158.67
H_{CH_3}	60.40	63.20	61.88	63.18	NA	65.52	NA	58.45	NA	62.99	62.64	59.59	58.82
H_{CH_3}	60.37	62.10	60.74	65.39	59.46	61.24	60.80	58.46	NA	61.04	63.77	59.31	59.98
H_{CH_3}	67.01	62.93	61.80	64.27	75.10	67.72	61.84	80.15	61.58	61.00	62.35	57.97	60.25
C_{CO}	107.86		105.37	112.13	104.30	107.03	108.48	104.46		100.56	104.17	104.97	106.88
O_{CO}	123.33		121.91	123.52	122.83	122.85	124.08	122.29		121.32	123.76	122.10	121.04

N_IAS(A)													
	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	3.96	3.93	5.11	5.15	3.55	3.98	4.21	3.81	1.04	4.81	4.79	4.38	4.45
C_{ipso}	4.52	3.77	3.75	3.80	2.07	5.09	1.84	4.46	3.79	3.73	3.83	4.25	3.66
C_{ortho}	4.13	4.01	4.01	4.03	3.98	4.00	3.96	4.09	3.99	4.02	4.00	4.04	4.01
C_{meta}	3.82	3.80	3.79	3.79	3.77	3.80	3.78	3.89	3.83	3.84	3.84	3.84	3.82
C_{para}	3.75	3.77	3.75	3.77	3.73	3.74	3.75	3.73	3.74	3.74	3.74	3.74	3.74
H_{phenyl}	0.97	0.97	0.97	0.97	1.01	1.01	1.02	1.01	0.98	0.99	0.99	0.98	0.98
H_{phenyl}	0.97	0.97	0.97	0.97	NA	1.02	1.02	1.01	0.94	0.95	0.95	0.98	0.94
H_{phenyl}	0.95	0.95	0.95	0.96	0.93	0.94	0.94	0.94	0.98	0.99	0.99	0.94	0.98
P/S	4.33	4.33	4.40	4.47	2.02	2.15	1.98	1.94	NA	1.98	1.97	1.96	1.96
C_{CH_3}	4.08	4.09	4.11	4.11	2.08	4.16	1.96	4.25	0.97	4.10	4.12	4.45	4.00
H_{CH_3}	1.02	1.02	1.02	0.98	0.11	1.13	0.06	1.02	NA	1.03	1.01	1.02	0.99
H_{CH_3}	1.02	0.97	1.01	1.07	0.97	0.96	0.95	1.02	NA	1.00	1.07	1.02	0.98
H_{CH_3}	1.27	1.02	1.02	1.10	1.19	1.13	1.13	1.60	0.97	1.00	0.98	1.04	0.98
C_{CO}	3.04		2.81	2.86	3.01	2.95	3.13	2.98		2.78	2.68	2.85	3.45
O_{CO}	1.69		1.71	1.73	1.69	1.70	1.70	1.69		1.71	1.73	1.70	1.73

G_IAS(A)													
	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh	2.75	2.67	3.51	3.57	2.60	2.92	3.23	2.83	0.76	3.49	3.43	3.24	3.23
C_{ipso}	3.05	2.52	2.50	2.54	1.42	3.45	1.23	2.97	2.55	2.51	2.57	2.88	2.43
C_{ortho}	2.73	2.63	2.63	2.65	2.63	2.65	2.58	2.71	2.64	2.65	2.65	2.68	2.64
C_{meta}	2.39	2.37	2.36	2.36	2.36	2.38	2.36	2.45	2.39	2.40	2.40	2.40	2.38
C_{para}	2.32	2.34	2.32	2.34	2.32	2.33	2.34	2.32	2.33	2.33	2.33	2.33	2.32
H_{phenyl}	0.52	0.52	0.52	0.52	0.56	0.56	0.57	0.56	0.53	0.54	0.54	0.53	0.53
H_{phenyl}	0.52	0.52	0.52	0.52	NA	0.56	0.57	0.56	0.50	0.50	0.50	0.53	0.50
H_{phenyl}	0.50	0.51	0.51	0.51	0.49	0.50	0.50	0.50	0.53	0.54	0.54	0.50	0.53
P/S	2.76	2.82	2.85	2.92	1.22	1.35	1.18	1.15	NA	1.19	1.19	1.19	1.19
C_{CH_3}	2.41	2.44	2.43	2.43	1.18	2.46	1.10	2.55	0.53	2.41	2.43	2.71	2.33
H_{CH_3}	0.58	0.57	0.57	0.54	0.08	0.66	0.05	0.58	NA	0.57	0.56	0.57	0.54
H_{CH_3}	0.58	0.53	0.55	0.61	0.54	0.53	0.53	0.58	NA	0.55	0.60	0.57	0.54
H_{CH_3}	0.78	0.57	0.57	0.63	0.70	0.68	0.67	1.08	0.53	0.55	0.54	0.59	0.54
C_{CO}	3.26		3.16	3.22	3.29	3.25	3.37	3.27		3.20	3.10	3.20	3.57
O_{CO}	2.22		2.30	2.33	2.25	2.26	2.23	2.25		2.33	2.35	2.29	2.24

Table S2. Electron density Bond Critical Point (BCP) analysis of molecular structure of the PCP and SCS complexes

Electron Density, ρ_b

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	0.05	0.15	0.13	0.14	0.05	0.07	0.02	0.04	0.15	0.12	0.15	0.12	0.12
C_{ipso}-C_{ortho}	0.29	0.30	0.29	0.30	0.29	0.27	0.29	0.29	0.29	0.29	0.30	0.29	0.29
Rh-P/S	0.10	0.10	0.10	0.10	0.08	0.08	0.08	0.08	0.08	0.09	0.08	0.08	0.09
C_{ipso}-C_{CH_3}	0.10	0.14	0.12	0.12			0.25		0.14	0.13	0.13	0.09	0.08
Rh-C_{CO}	0.18		0.13	0.13	0.18	0.17	0.19	0.18		0.13	0.11	0.15	0.21
C-O	0.47		0.48	0.48	0.47	0.47	0.47	0.47		0.48	0.48	0.48	0.47

Hamiltonian form of kinetic energy density, K(r)

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	0.01	0.07	0.06	0.06	0.01	0.02	0.00	0.01	0.08	0.05	0.07	0.05	0.05
C_{ipso}-C_{ortho}	0.26	0.27	0.26	0.28	0.25	0.23	0.26	0.26	0.26	0.26	0.26	0.25	0.26
Rh-P/S	0.04	0.04	0.04	0.04	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03
C_{ipso}-C_{CH_3}		0.07	0.05	0.06					0.07	0.06	0.06	0.03	0.03
Rh-C_{CO}	0.11		0.06	0.05	0.10	0.09	0.12	0.10		0.06	0.04	0.07	0.13
C-O	0.84		0.86	0.87	0.84	0.85	0.84	0.84		0.87	0.87	0.86	0.84

Cremer and Kraka energy density H(r) = G(r) + V(r) = -K(r)

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	-0.01	-0.07	-0.06	-0.06	-0.01	-0.02	0.00	-0.01	-0.08	-0.05	-0.07	-0.05	-0.05
C_{ipso}-C_{ortho}	-0.26	-0.27	-0.26	-0.28	-0.25	-0.23	-0.26	-0.26	-0.26	-0.26	-0.26	-0.25	-0.26
Rh-P/S	-0.04	-0.04	-0.04	-0.04	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.03
C_{ipso}-C_{CH_3}		-0.07	-0.05	-0.06					-0.07	-0.06	-0.06	-0.03	-0.03
Rh-C_{CO}	-0.11		-0.06	-0.05	-0.10	-0.09	-0.12	-0.10		-0.06	-0.04	-0.07	-0.13
C-O	-0.84		-0.86	-0.87	-0.84	-0.85	-0.84	-0.84		-0.87	-0.87	-0.86	-0.84

Laplacian of electron density $\nabla^2\rho_b$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	0.15	0.08	0.13	0.06	0.14	0.15	0.05	0.13	0.12	0.18	0.10	0.13	0.16
C_{ipso}-C_{ortho}	**-0.67**	**-0.69**	**-0.68**	**-0.71**	**-0.64**	**-0.59**	**-0.67**	**-0.67**	**-0.67**	**-0.67**	**-0.68**	**-0.66**	**-0.67**
Rh-P/S	0.11	0.13	0.10	0.10	0.18	0.18	0.19	0.18	0.20	0.19	0.17	0.18	0.18
C_{ipso}-C_{CH_3}	0.11	0.04	0.03	0.08			-0.54		0.03	0.02	0.05	0.16	0.13
Rh-C_{CO}	0.46		0.46	0.45	0.46	0.47	0.49	0.45		0.45	0.42	0.46	0.30
C-O	1.00		1.12	1.13	1.08	1.06	0.96	1.09		1.21	1.17	1.12	1.00

Bond ellipticity $\varepsilon = \lambda_1/\lambda_2 - 1$ ($|\lambda_1| \geq |\lambda_2|$)

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	0.19	0.06	0.04	0.03	0.43	0.31	0.05	0.38	0.07	0.03	0.03	0.00	0.05
C_{ipso}-C_{ortho}	0.18	0.19	0.17	0.21	0.16	0.12	0.17	0.18	0.16	0.13	0.17	0.16	0.14
Rh-P/S	0.05	0.02	0.04	0.02	0.06	0.11	0.07	0.02	0.07	0.02	0.03	0.06	0.07
C_{ipso}-C_{CH_3}	0.05	0.01	0.01	0.01			0.03		0.01	0.03	0.01	0.23	0.33
Rh-C_{CO}	0.01		0.03	0.03	0.03	0.03	0.07	0.08		0.02	0.01	0.04	0.16
C-O	0.01		0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.02

Electrostatic Potential from Nuclei V_{nuc}

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	47.79	48.03	49.76	50.16	49.67	53.52	48.28	48.95	50.65	51.94	52.87	52.14	51.43
C_{ipso}-C_{ortho}	40.74	39.33	40.59	41.47	43.40	45.80	44.77	43.24	42.36	43.47	44.38	44.22	43.28
Rh-P/S	48.42	46.00	48.41	48.32	49.32	52.69	51.96	49.22	47.20	49.66	49.41	49.52	49.73
C_{ipso}-C_{CH_3}	39.79	44.70	46.65	47.18					46.49	48.41	48.82	49.49	46.22
Rh-C_{CO}	49.59		48.40	49.22	50.53	53.40	54.06	50.43		49.45	49.95	50.53	51.91
C-O	40.81		40.06	41.39	41.32	43.96	44.67	41.37		40.67	42.26	41.99	43.13

Electron-nuclear attractive contribution to virial field V, V_{en}

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	-2.48	-7.16	-6.41	-6.84	-2.26	-3.52	-1.10	-2.18	-7.83	-6.42	-7.82	-6.51	-6.14
C_{ipso}-C_{ortho}	-11.90	-11.66	-11.94	-12.54	-12.43	-12.55	-13.17	-12.65	-12.43	-12.78	-13.11	-12.84	-12.77
Rh-P/S	-4.79	-4.58	-4.90	-4.66	-3.84	-4.17	-4.19	-3.95	-3.99	-4.24	-3.95	-4.04	-4.40
C_{ipso}-C_{CH_3}	-4.79	-6.15	-5.68	-5.83			-10.82		-6.58	-6.11	-6.47	-4.40	-3.83
Rh-C_{CO}	-9.16		-6.45	-6.35	-9.27	-8.93	-10.48	-9.24		-6.52	-5.63	-7.70	-10.70
C-O	-19.01		-19.18	-19.87	-19.45	-20.77	-20.81	-19.49		-19.69	-20.47	-20.07	-20.12

Repulsive contribution to virial field V, $V_{rep} = V - V_{en}$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	2.43	6.99	6.26	6.70	2.21	3.45	1.08	2.13	7.65	6.27	7.65	6.37	6.00
C_{ipso}-C_{ortho}	11.56	11.30	11.59	12.16	12.09	12.25	12.81	12.30	12.08	12.42	12.75	12.50	12.41
Rh-P/S	4.69	4.47	4.79	4.56	3.76	4.09	4.10	3.86	3.89	4.14	3.86	3.95	4.30
C_{ipso}-C_{CH_3}	4.69	6.01	5.57	5.70			10.56		6.43	5.99	6.33	4.30	3.74
Rh-C_{CO}	8.84		6.22	6.13	8.95	8.64	10.13	8.92		6.29	5.45	7.44	10.36
C-O	17.09		17.18	17.86	17.49	18.80	18.89	17.53		17.65	18.43	18.06	18.18

Laplacian of the electron-nuclear attractive contribution to virial field V_{en}, $\nabla^2 V_{en}$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	-7.20	-3.93	-6.30	-2.80	-6.73	-8.02	-2.64	-6.49	-5.92	-9.16	-5.22	-7.00	-8.13
C_{ipso}-C_{ortho}	27.34	27.07	27.48	29.51	27.80	27.15	30.12	28.83	28.41	29.26	30.01	29.03	29.18
Rh-P/S	-5.12	-5.76	-4.85	-5.06	-9.03	-9.29	-9.72	-9.03	-9.60	-9.27	-8.64	-8.89	-8.87
C_{ipso}-C_{CH_3}	-5.12	-1.79	-1.29	-3.76					-1.63	-1.14	-2.60	-8.06	-5.84
Rh-C_{CO}	-22.92		-22.29	-22.39	-23.42	-24.88	-26.60	-22.72		-22.48	-21.00	-23.15	-15.79
C-O	-40.77		-45.06	-46.75	-44.56	-46.81	-42.73	-44.98		-49.21	-49.65	-47.14	-43.03

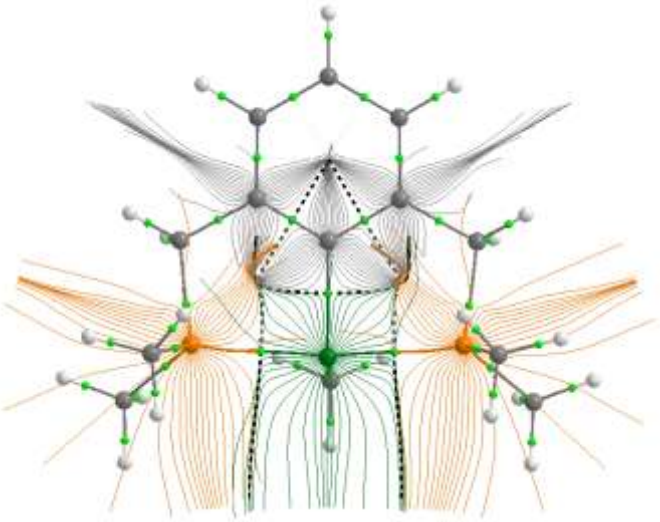
Laplacian of the repulsive contribution to virial field V_{rep}, $\nabla^2 V_{rep}$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	6.70	2.57	5.16	1.65	6.29	7.42	2.56	6.14	4.42	7.94	3.84	5.92	7.05
C_{ipso}-C_{ortho}	-30.24	-30.07	-30.43	-32.67	-30.61	-29.69	-33.13	-31.78	-31.38	-32.25	-33.05	-31.94	-32.22
Rh-P/S	4.37	4.95	4.09	4.33	8.22	8.50	8.89	8.20	8.68	8.37	7.80	8.03	7.97
C_{ipso}-C_{CH_3}	4.38	0.61	0.35	2.74					0.39	0.14	1.53	7.19	5.13
Rh-C_{CO}	20.72		20.70	20.85	21.23	22.93	24.21	20.54		20.86	19.65	21.36	13.31
C-O	21.27		24.07	25.60	24.29	26.49	23.61	24.63		27.44	27.96	26.22	23.90

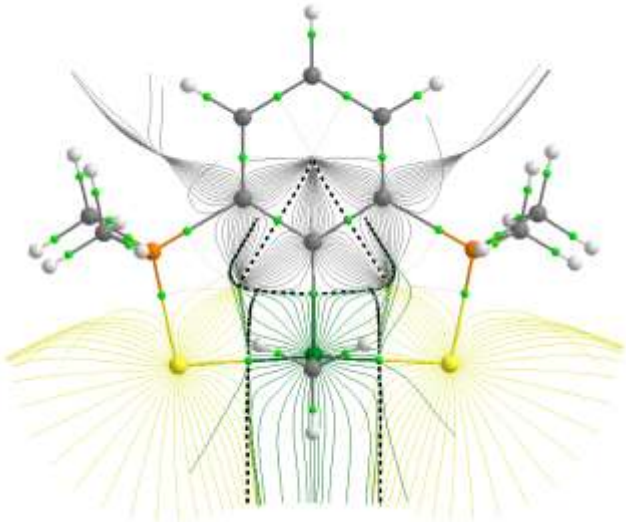
Laplacian of the Hamiltonian form of kinetic energy density, $\nabla^2 K(r)$

	PCP complexes				SCS complexes								
	23	**15**	**17**	**16**	**19**	**19-S**	**19-S1**	**20**	**11**	**13**	**12**	**TS2**	**TS1**
Rh-C_{ipso}	0.05	0.14	0.06	0.11	0.04	0.07	0.03	0.05	0.14	0.07	0.14	0.14	0.09
C_{ipso}-C_{ortho}	1.61	1.70	1.67	1.81	1.55	1.35	1.71	1.66	1.69	1.70	1.74	1.64	1.73
Rh-P/S	0.13	0.13	0.12	0.12	0.15	0.15	0.16	0.16	0.16	0.16	0.14	0.15	0.17
C_{ipso}-C_{CH_3}	0.13	0.10	0.07	0.04					0.12	0.09	0.04	0.07	0.05
Rh-C_{CO}	0.61		0.29	0.28	0.57	0.48	0.63	0.54		0.26	0.23	0.35	0.73
C-O	-28.23		-29.85	-30.15	-28.82	-29.18	-28.09	-28.87		-30.44	-30.69	-29.77	-27.86

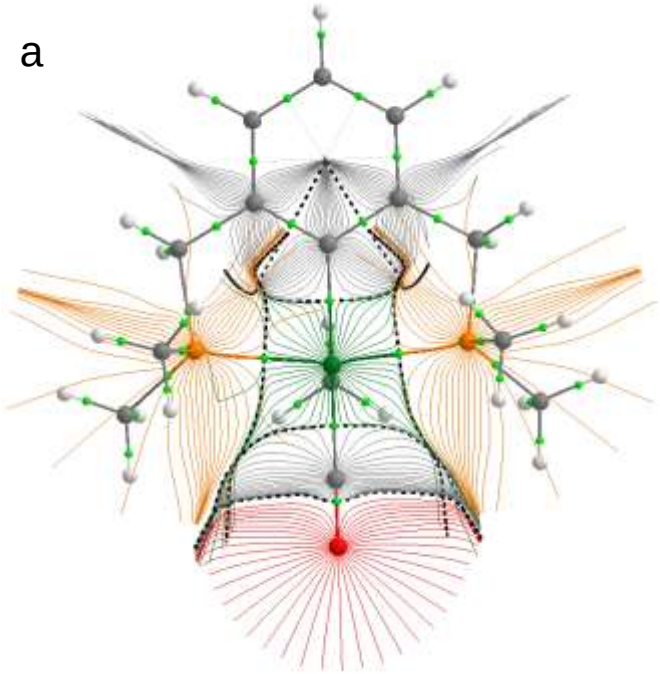
QTAIM pictures of aryl-methyl PCP and SCS complexes



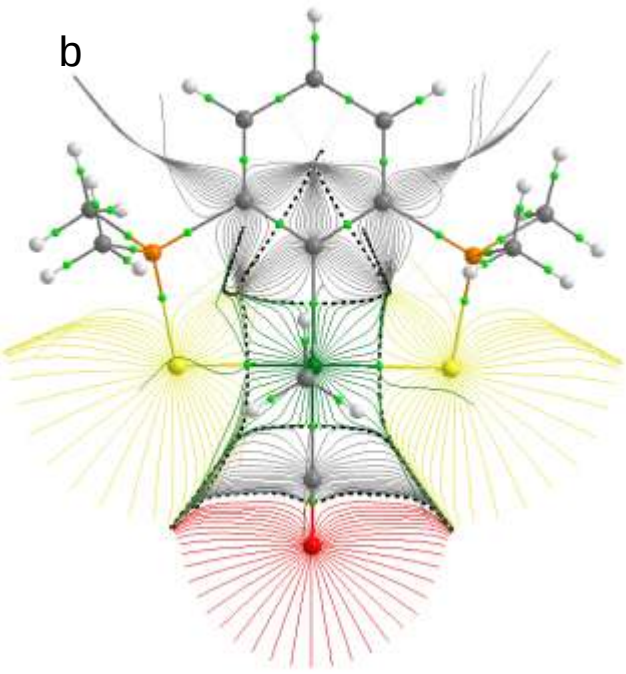
PCP-Rh-CH3



SCS-Rh-CH3

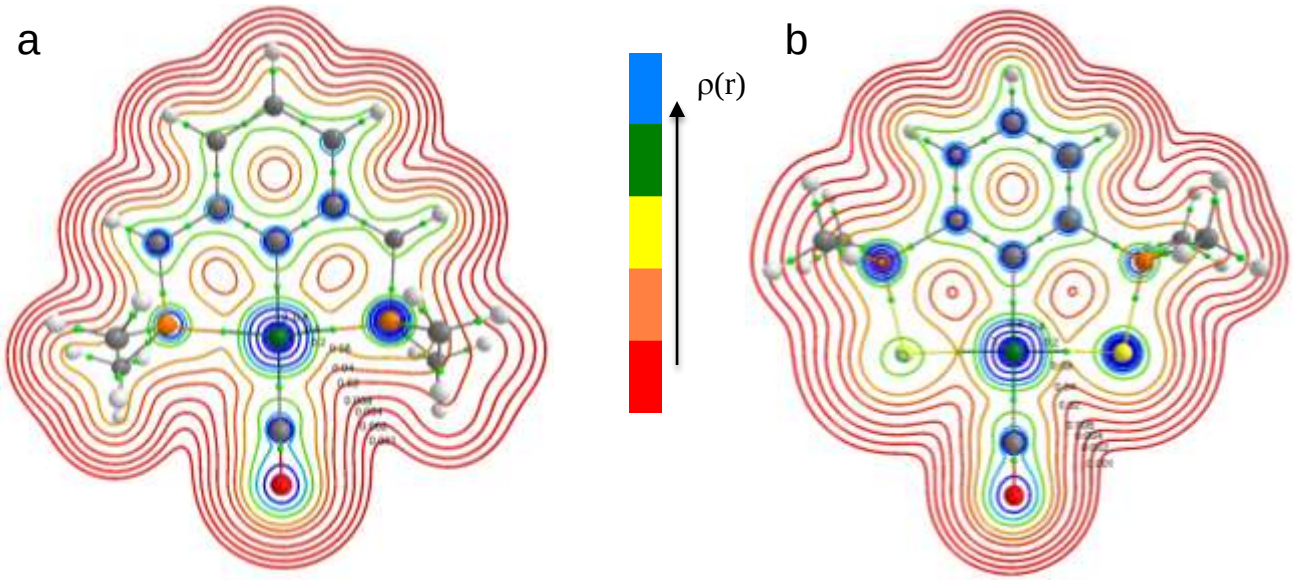


PCP-Rh-CH3-CO

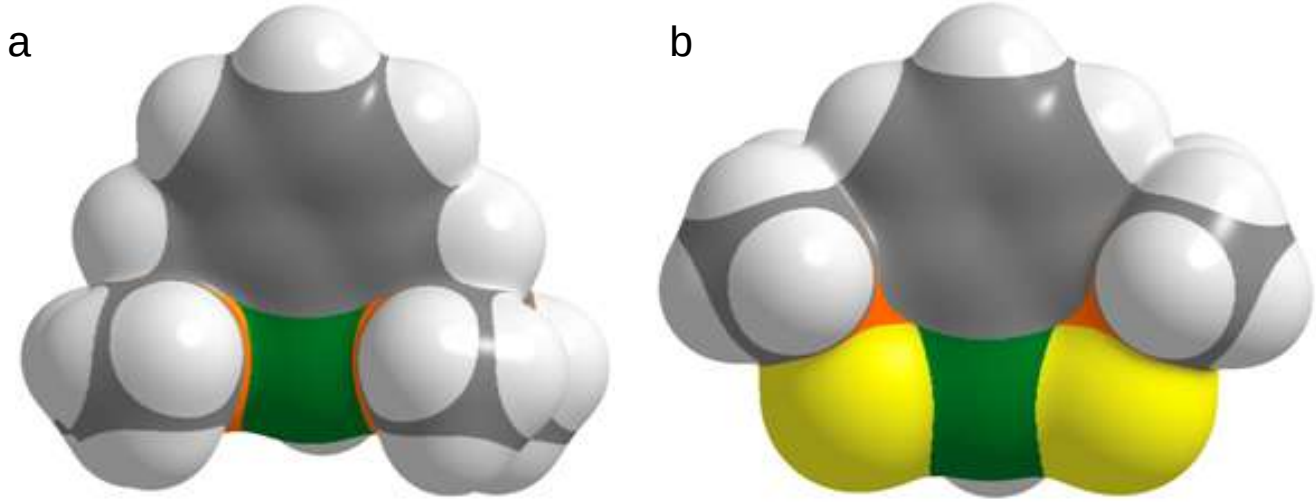


SCS-Rh-CH3-CO

Basin path + IAS EV path for complexes **17** (a) and **13** (b).

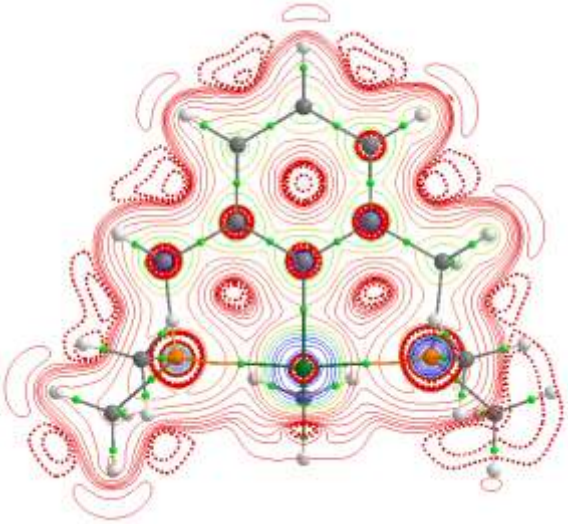


Counter maps of electron density ρ(r) for complexes **17** (a) and **13** (b).

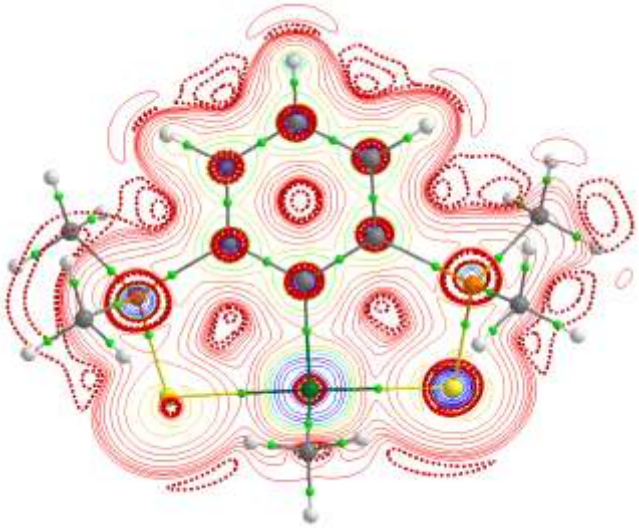


3D Laplasian of electron density for complexes **15** (a) and **11** (b). Resolution 0.05, isosurface 0.01

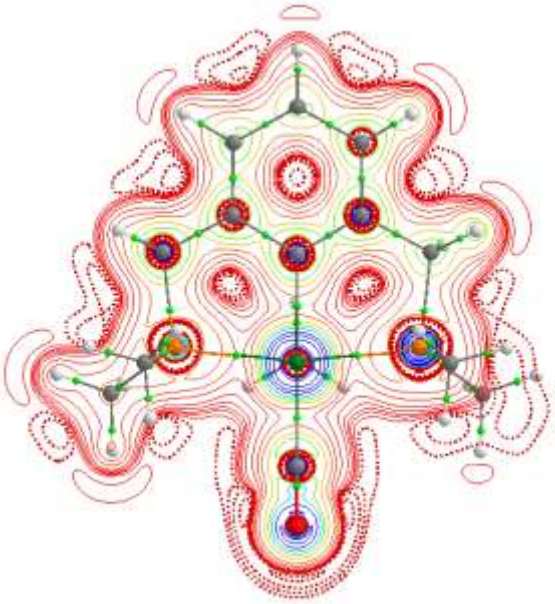
The Hamiltonian form of the electron kinetic energy density K(=-H). Min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



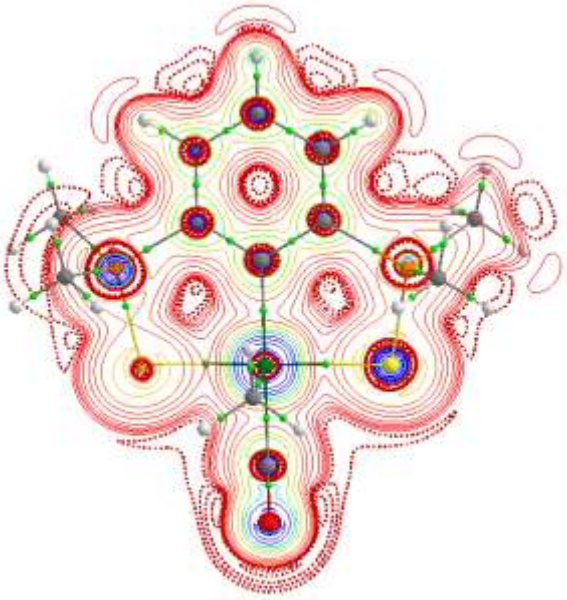
PCP-Rh-CH3



SCS-Rh-CH3



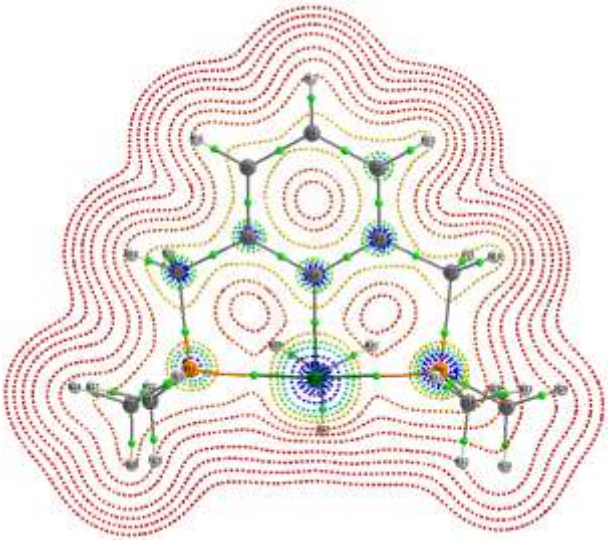
PCP-Rh-CH3-CO



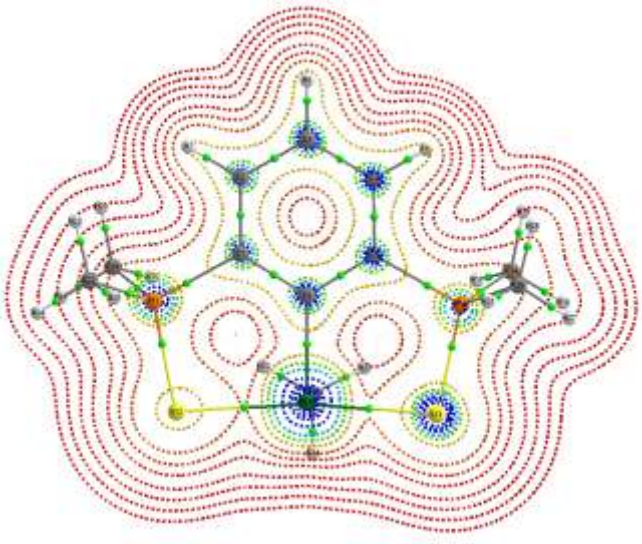
SCS-Rh-CH3-CO

Counter maps for molecular structure of the PCP and SCS complexes in three dimensions

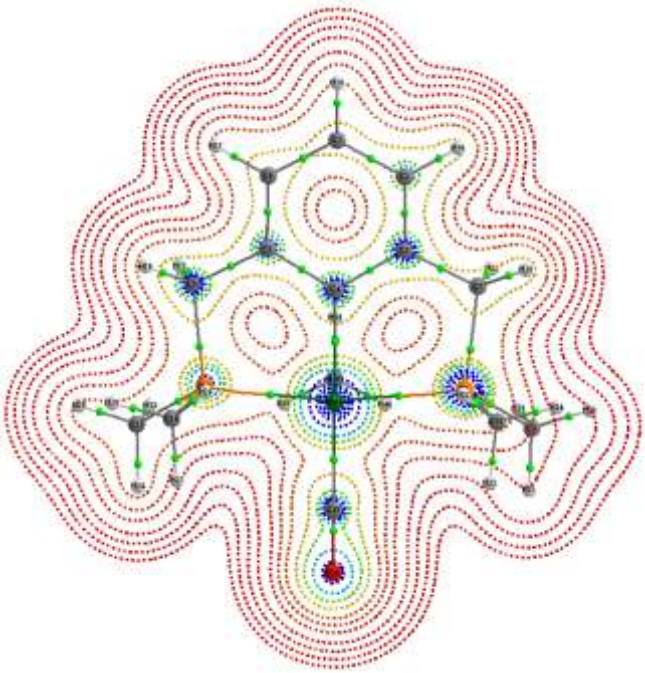
Rho, min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



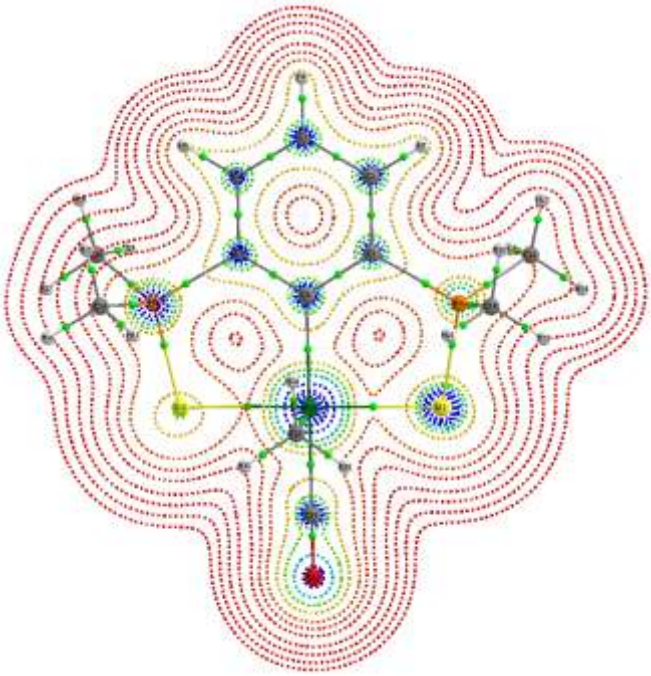
PCP-Rh-CH3



SCS-Rh-CH3

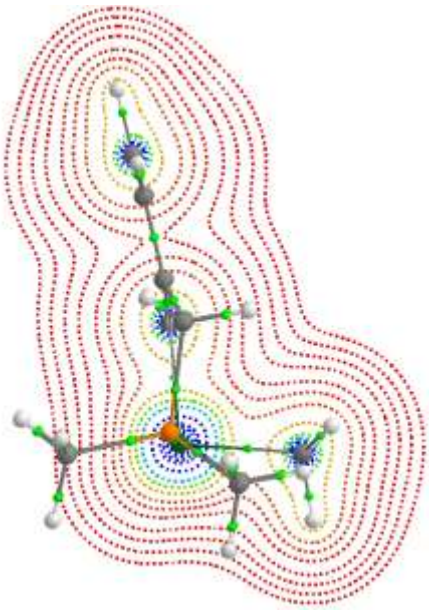


PCP-Rh-CH3-CO

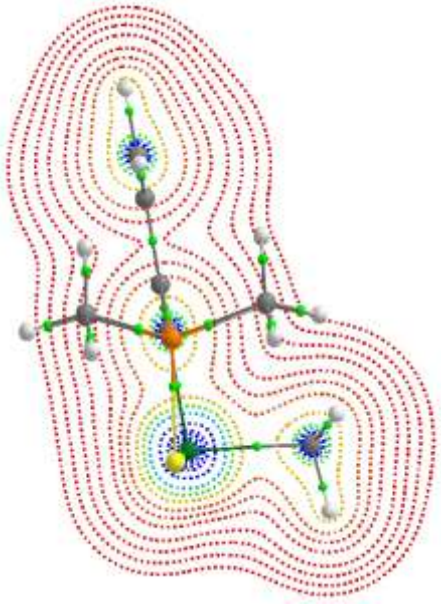


SCS-Rh-CH3-CO

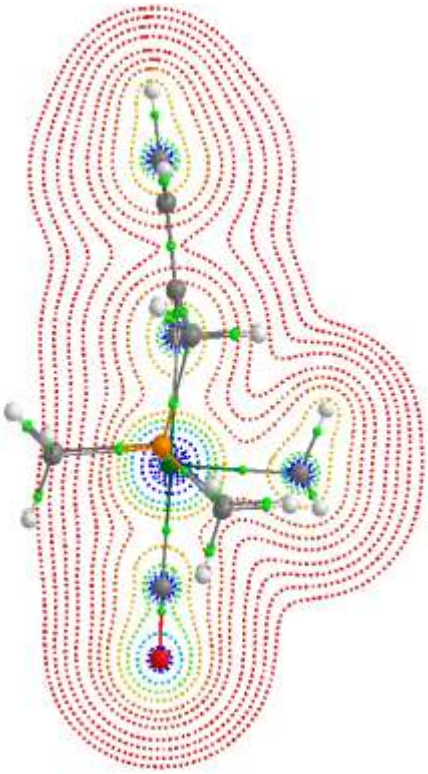
Rho, min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



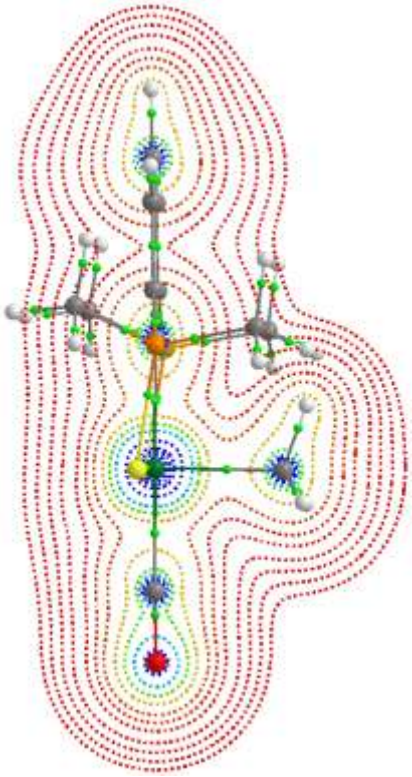
PCP-Rh-CH3



SCS-Rh-CH3

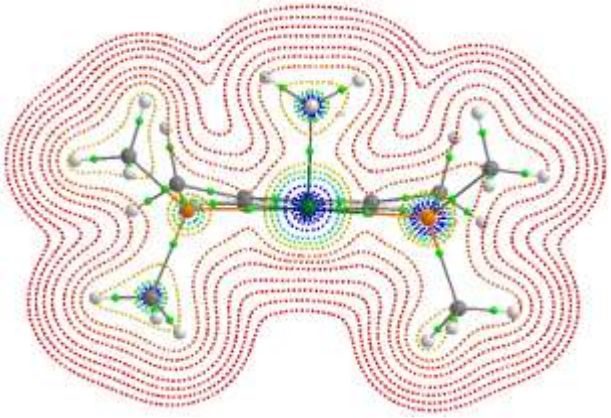


PCP-Rh-CH3-CO

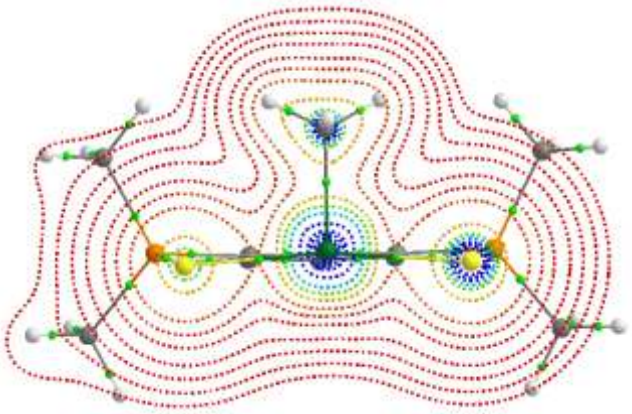


SCS-Rh-CH3-CO

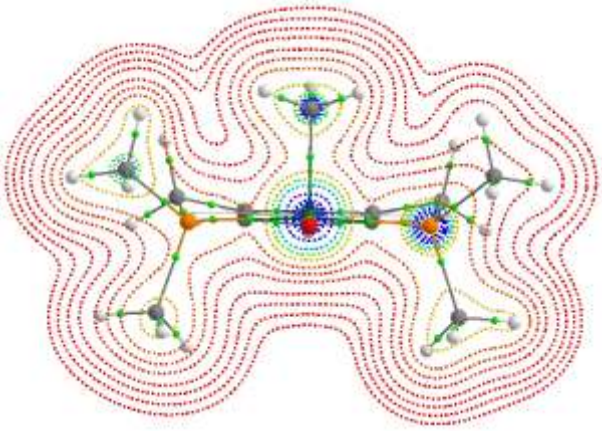
Rho, min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



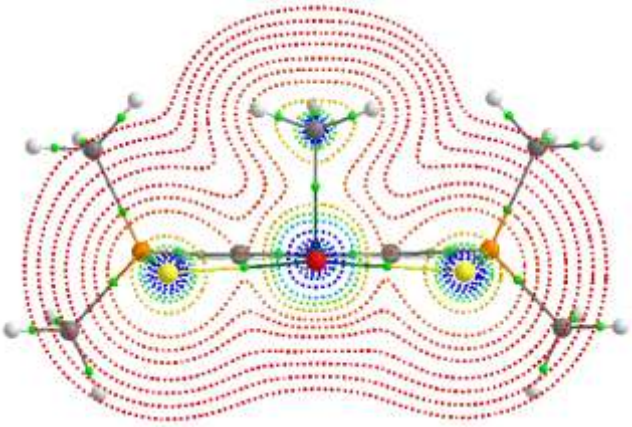
PCP-Rh-CH3



SCS-Rh-CH3

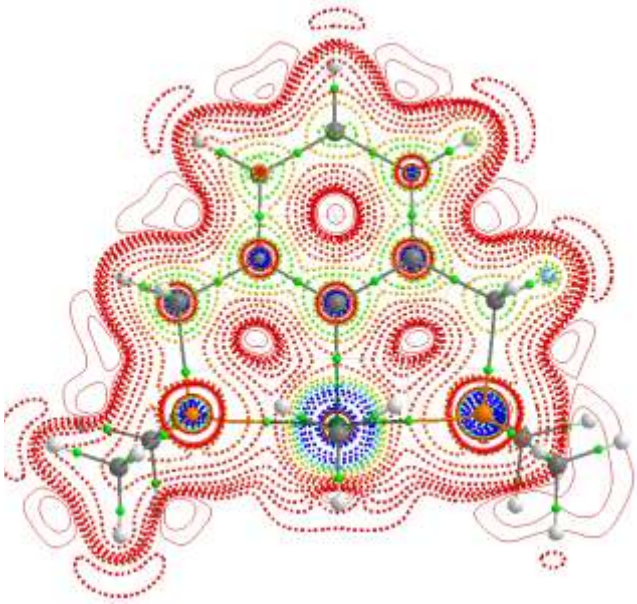


PCP-Rh-CH3-CO

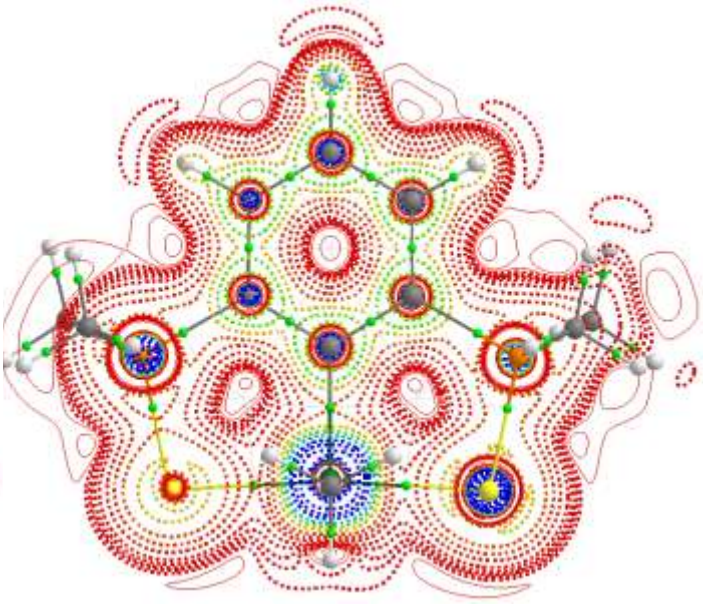


SCS-Rh-CH3-CO

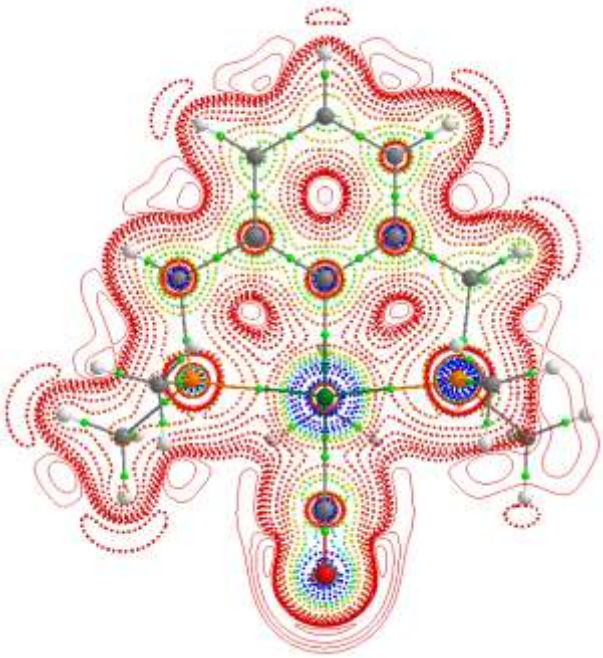
K, The Hamiltonian kinetic energy density; min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



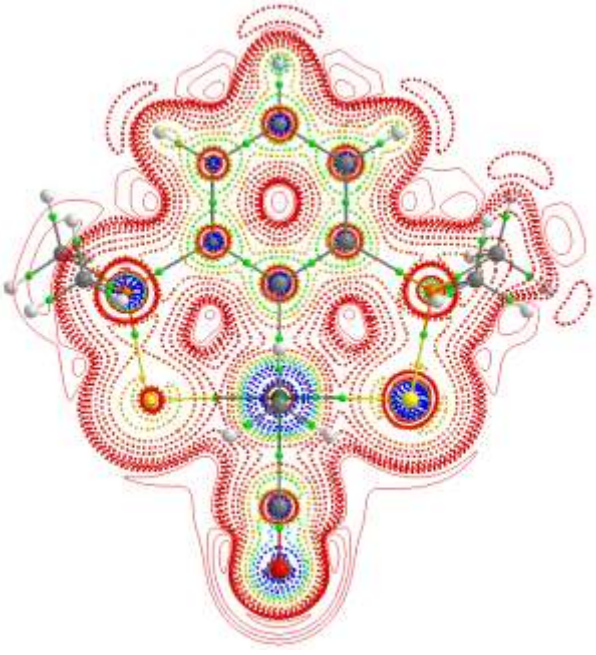
PCP-Rh-CH3



SCS-Rh-CH3

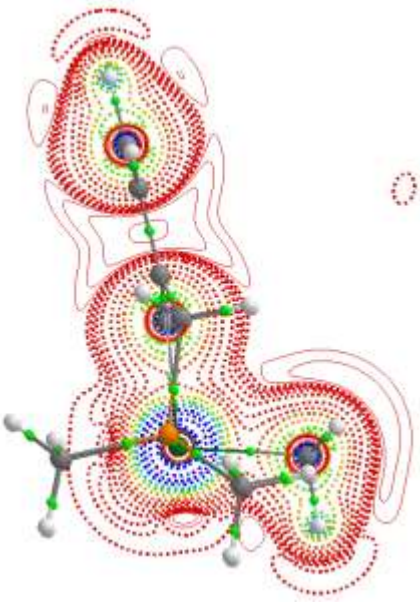


PCP-Rh-CH3-CO

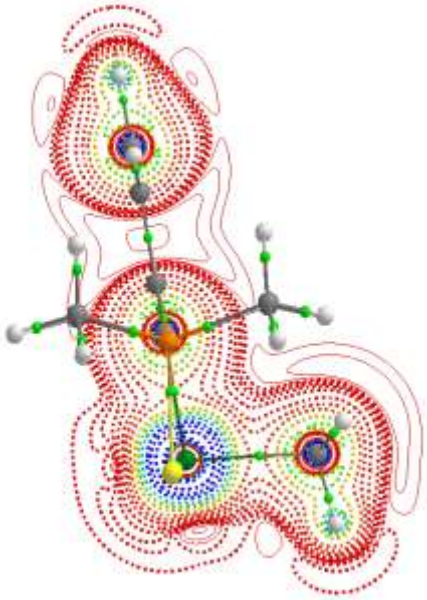


SCS-Rh-CH3-CO

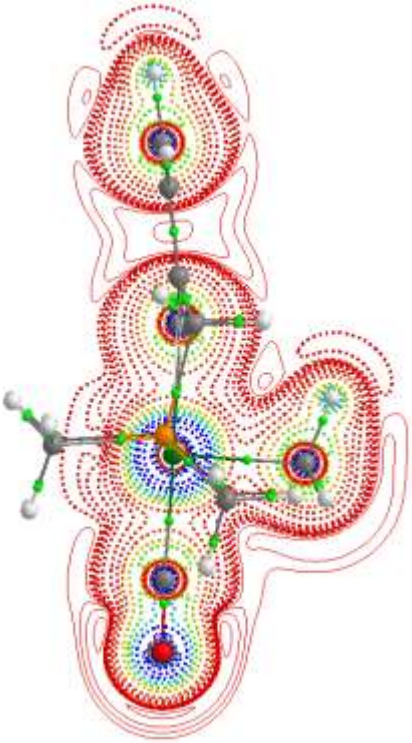
K, The Hamiltonian kinetic energy density; min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



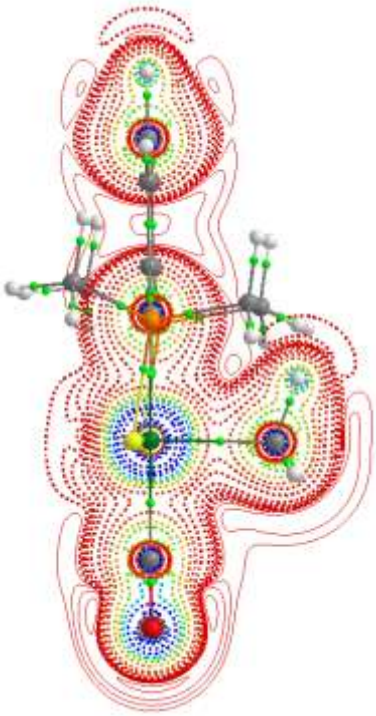
PCP-Rh-CH3



SCS-Rh-CH3

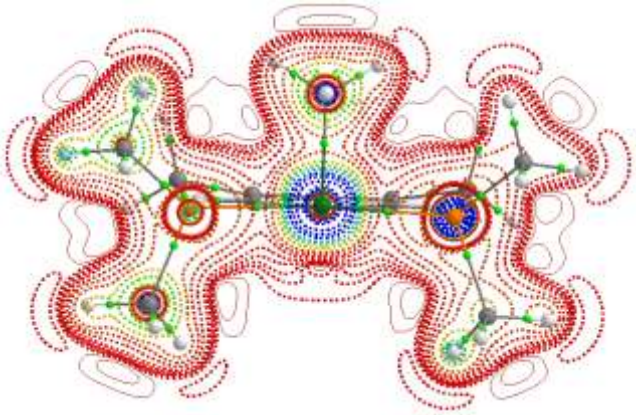


PCP-Rh-CH3-CO

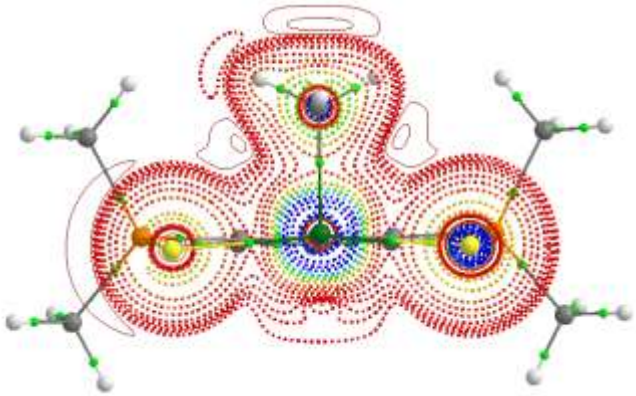


SCS-Rh-CH3-CO

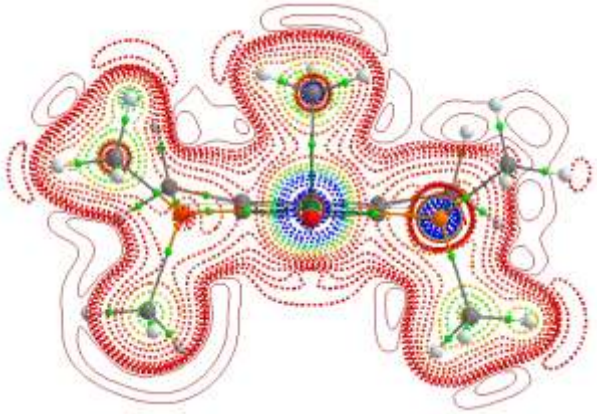
K, The Hamiltonian kinetic energy density; min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



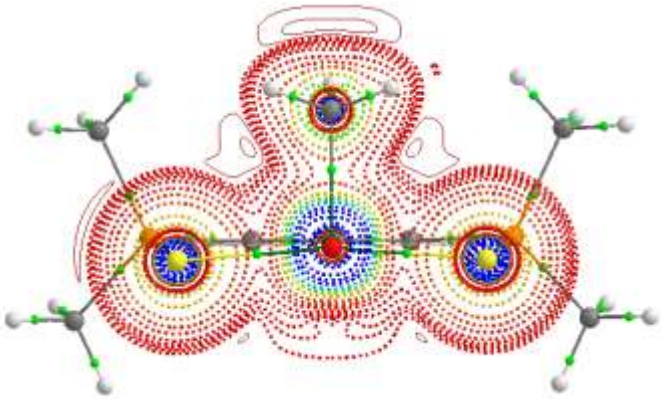
PCP-Rh-CH3



SCS-Rh-CH3

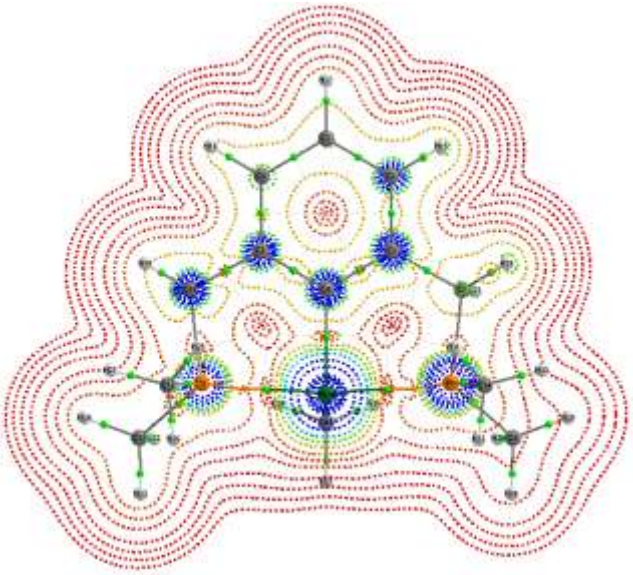


PCP-Rh-CH3-CO

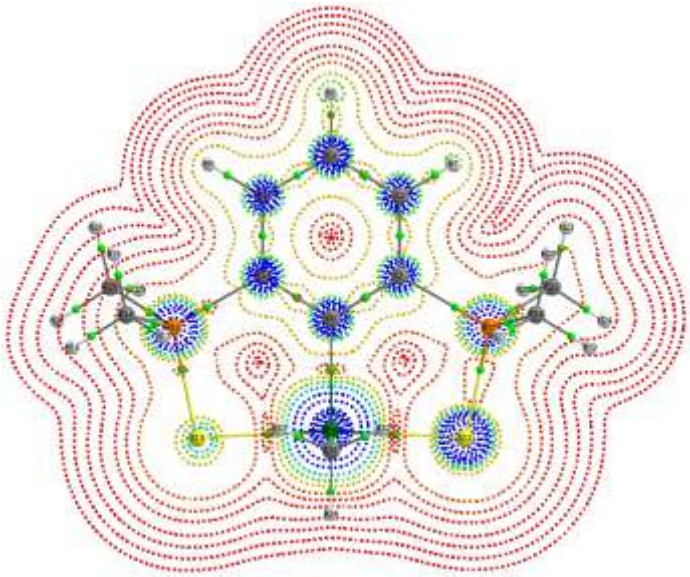


SCS-Rh-CH3-CO

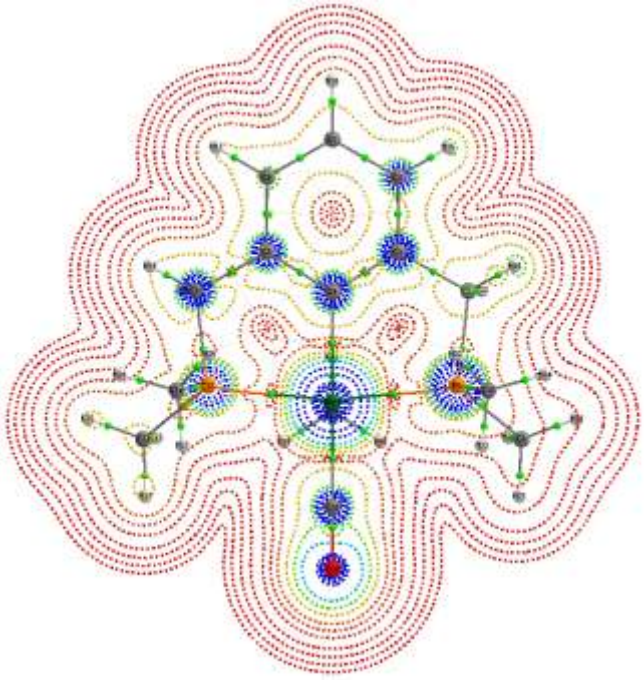
GRM, magnitude of the gradient of the electron density; min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



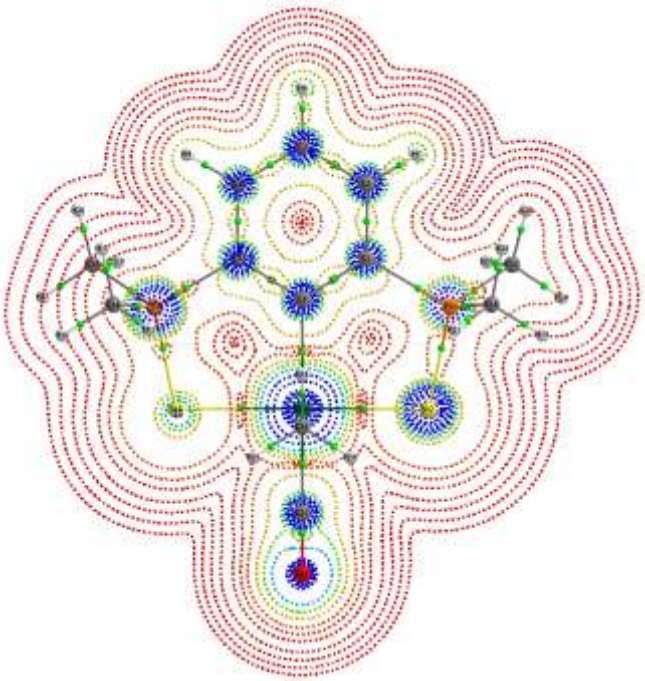
PCP-Rh-CH3



SCS-Rh-CH3

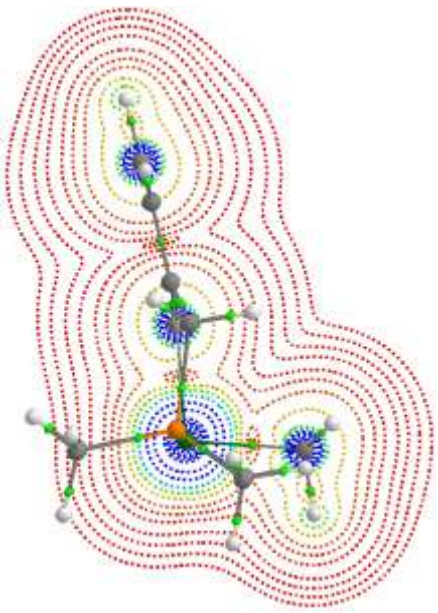


PCP-Rh-CH3-CO

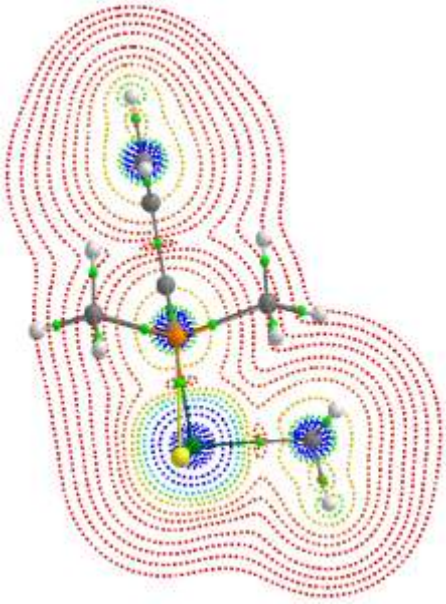


SCS-Rh-CH3-CO

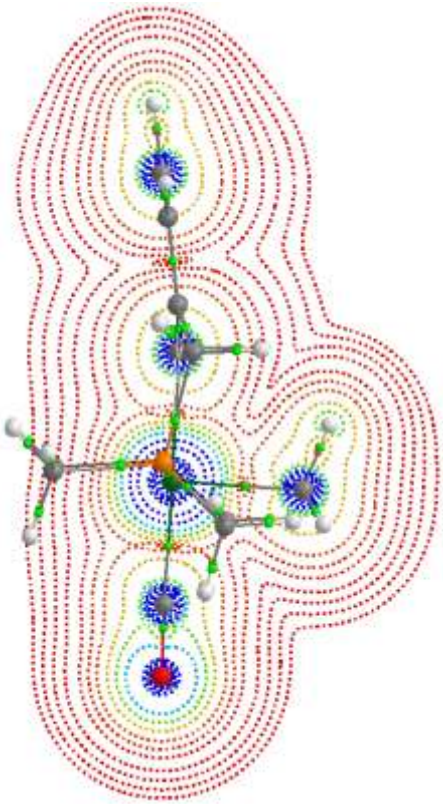
GRM, magnitude of the gradient of the electron density (|GradRho|); min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



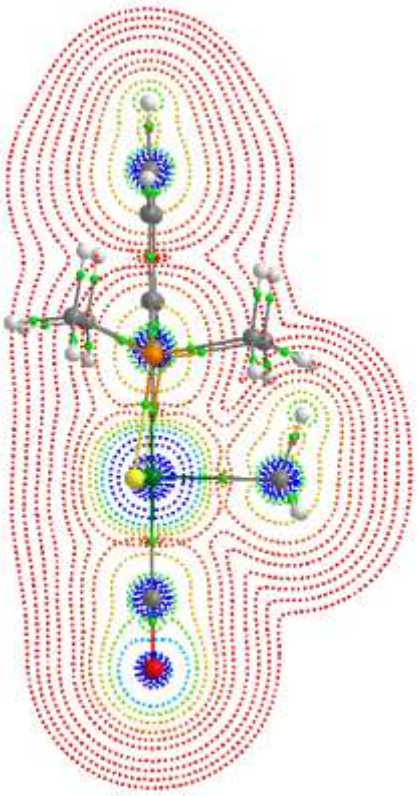
PCP-Rh-CH3



SCS-Rh-CH3

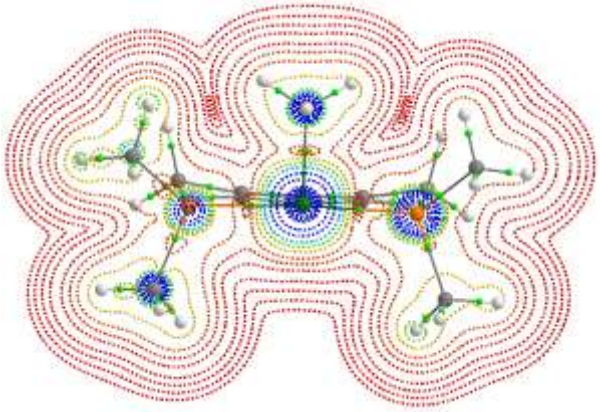


PCP-Rh-CH3-CO

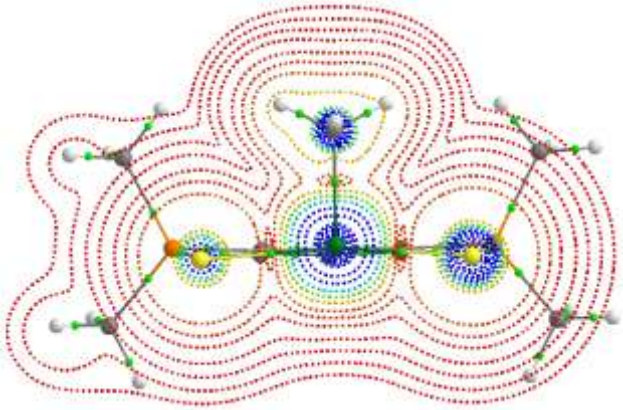


SCS-Rh-CH3-CO

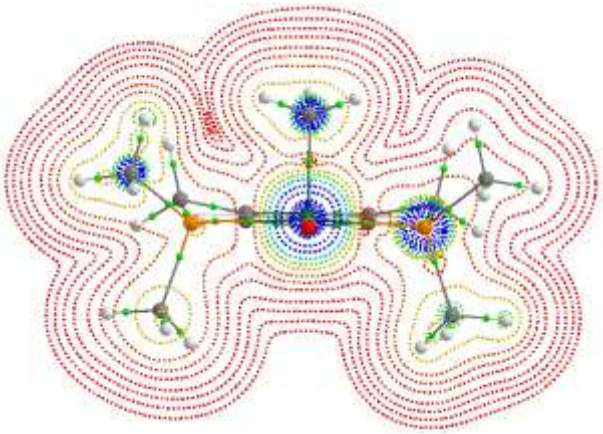
GRM, magnitude of the gradient of the electron density; min el. Dens=0.001, resolution 0.05, allow tubular; color scale 0-1



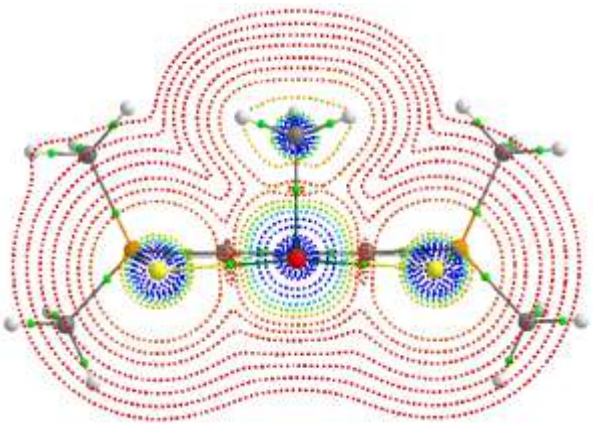
PCP-Rh-CH3



SCS-Rh-CH3

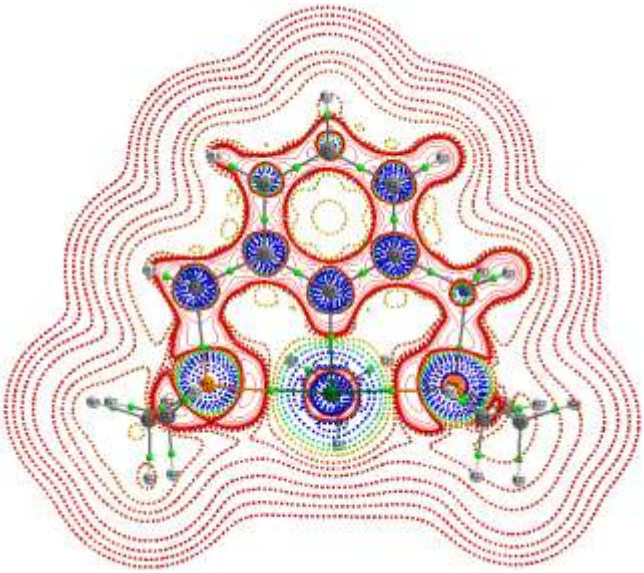


PCP-Rh-CH3-CO

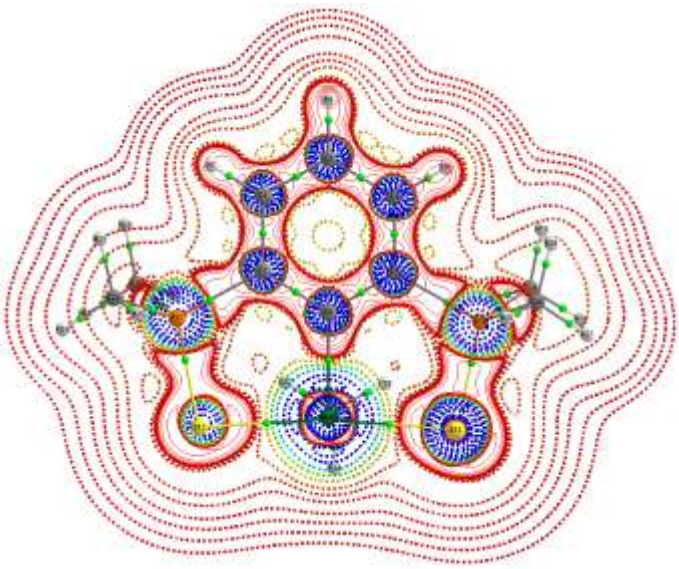


SCS-Rh-CH3-CO

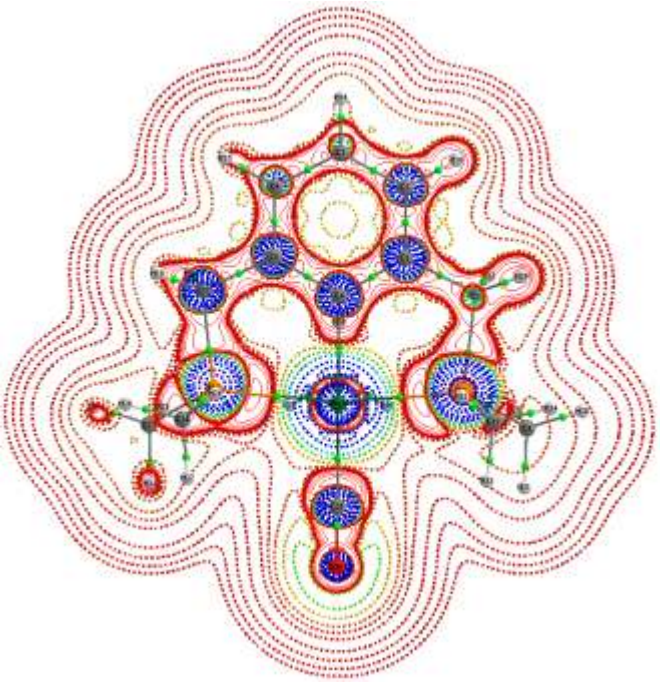
DelSqRho; min El. Dens=0.001; resolution 0.05; allow tubular; color scale 0-1



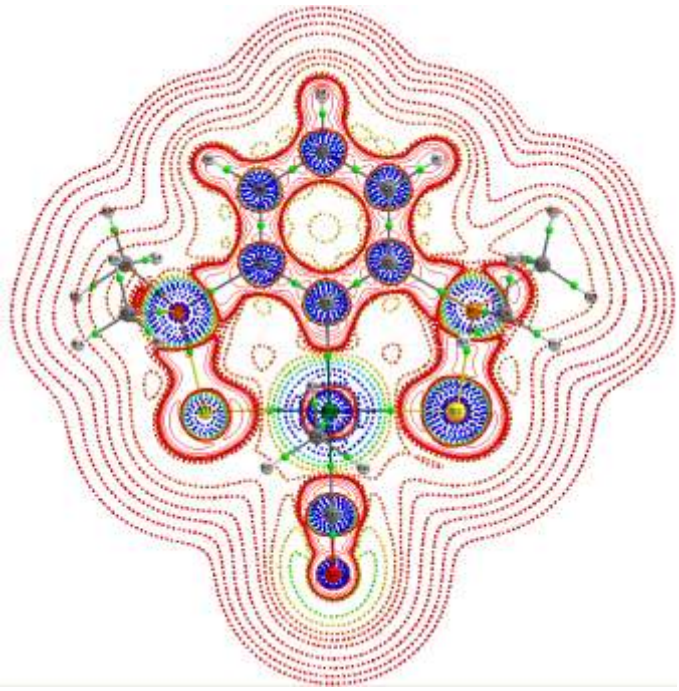
PCP-Rh-CH3



SCS-Rh-CH3

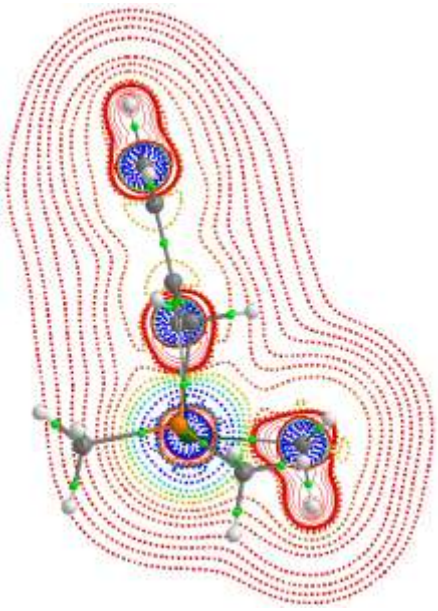


PCP-Rh-CH3-CO

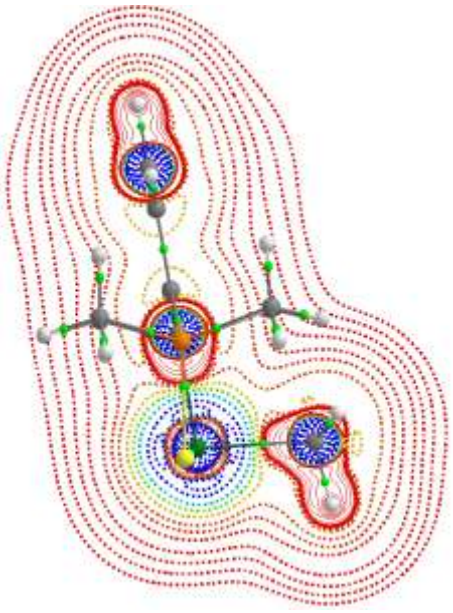


SCS-Rh-CH3-CO

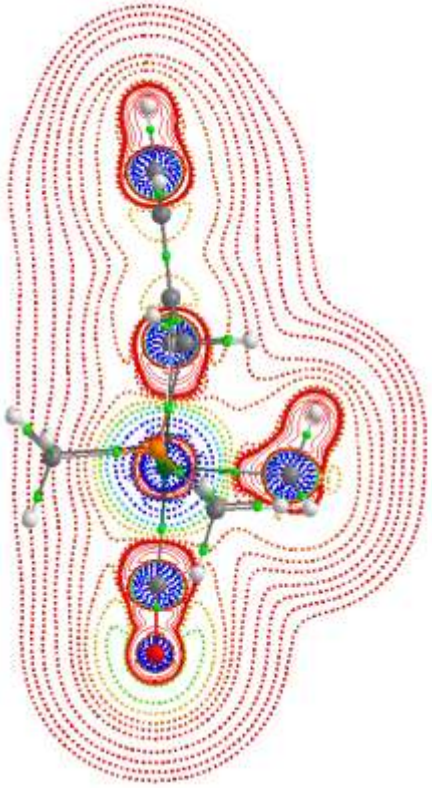
DelSqRho; min El. Dens=0.001; resolution 0.05; allow tubular; color scale 0-1



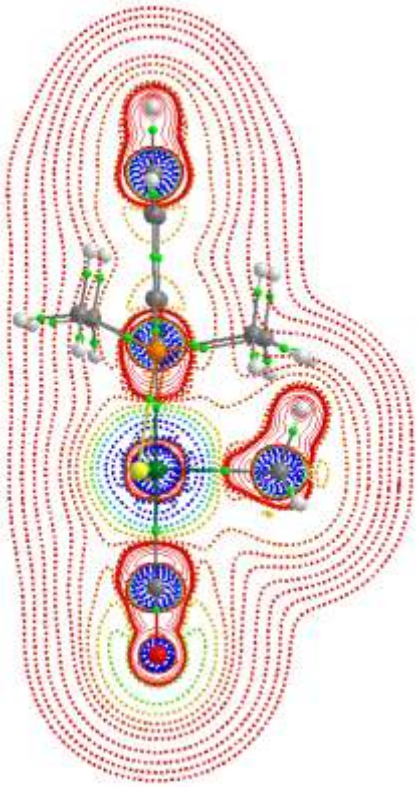
PCP-Rh-CH3



SCS-Rh-CH3

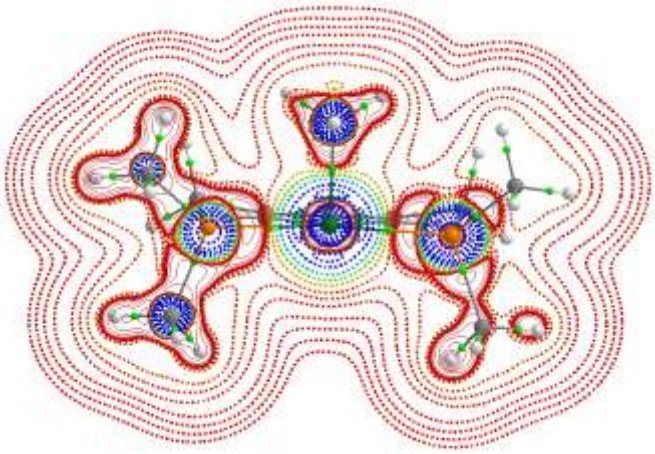


PCP-Rh-CH3-CO

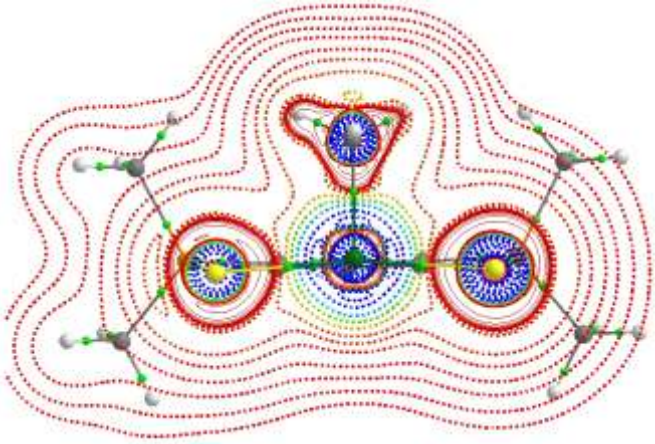


SCS-Rh-CH3-CO

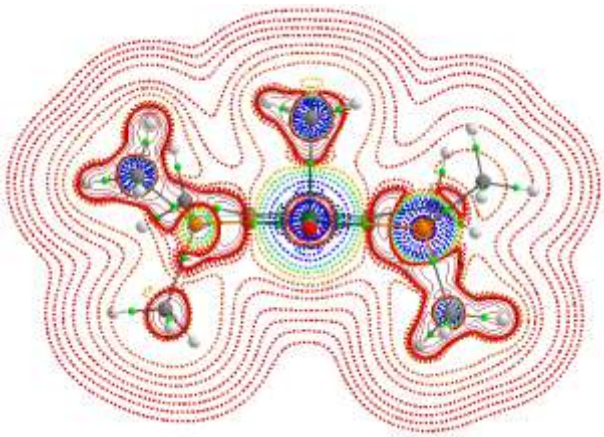
DelSqRho; min El. Dens=0.001; resolution 0.05; allow tubular; color scale 0-1



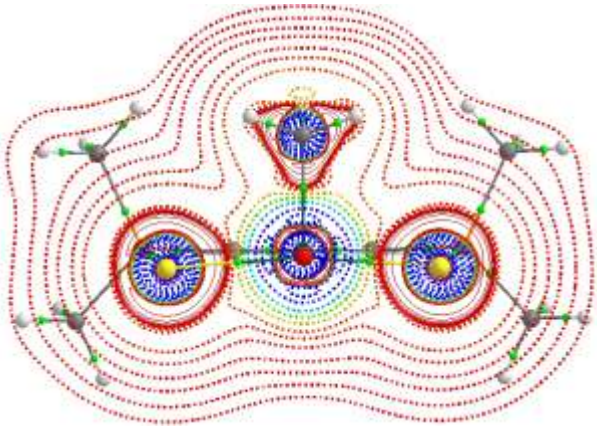
PCP-Rh-CH3



SCS-Rh-CH3



PCP-Rh-CH3-CO



SCS-Rh-CH3-CO