Electronic Supplementary Material

A ruthenium tellurocarbonyl (CTe) complex with a cyclopentadienyl ligand: Systematic studies of a series of the chalcogenocarbonyl complexes [CpRuCl(CE)(H_2IMes)] (E = O, S, Se, Te)

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General Considerations. All reactions were carried out under a dry inert gas atmosphere using standard Schlenk techniques unless otherwise noted. Chemical shifts are reported in δ, referenced to residual ^{1}H and ^{13}C signals of $CDCl_3$ as internal standards (δ 7.24 for ^{1}H NMR and δ 77.0 for ^{13}C NMR) or to the ^{125}Te signal of PhTeTePh (δ 422.0 relative to MeTeMe at δ 0) as an external standard. ATR-IR spectra were recorded on a JASCO FT/IR-4600 spectrometer with a diamond attenuated total reflectance unit. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer.

Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) of anhydrous grade were purchased from commercial sources and were degassed by three freeze-pump-thaw cycles before use. Hexane was distilled, degassed and stored over activated molecular sieves (4A). $CDCl_3$ was passed through a small column of neutral alumina, degassed by freeze-pump-thaw cycles, and stored over activated molecular sieves (4A). $[RuCl_2(CE)(H_2IMes)(dmap)_2]$ (**1-CE**) was obtained according to the literature.[S1] Cyclopentadienyllithium (CpLi) was purchased from Strem and stored in a Schlenk flask under an inert atmosphere. Triethyl borane (Et_3B) 1.0 M solution in hexane was used as received from Kanto Chemical Co., Inc.

[S1] Y. Mutoh, N. Kozono, M. Araki, N. Tsuchida, K. Takano and Y. Ishii, *Organometallics*, 2010, **29**, 519–522.

[CpRuCl(CTe)(H_2IMes)] (2-CTe). A solid mixture of CpLi (15 mg, 0.21 mmol, 1.5 equiv) and [$RuCl_2$(CTe)(H_2IMes)(dmap)$_2$] (**1-CTe**, 120.0 mg, 0.14 mmol) was allowed to cool to −20 °C. To this was added THF (4.5 mL) and Et_3B (1.0 M solution in hexane, 0.28 mL, 0.28 mmol, 2.0 equiv) at −20 °C, and the mixture was stirred at the temperature for 0.5 h. To this was added hexane (50 mL), and the resulting suspension was passed through a pad of Celite. The pad was washed with hexane (10 mL). The combined filtrate was stored in a freezer for 7 days to give [CpRuCl(CTe)(H_2IMes)] (**2-CTe**) (55.0 mg, 0.085 mmol, 61% yield) as red crystals. IR (cm^{-1}): 990 (ν_{CTe}). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.94, 6.93 (s, 2H each, Ar of Mes), 4.61 (s, 5H, Cp), 3.96 (s, 4H, N(CH_2)$_2$N), 2.39 (s, 6H, *p*-CH_3 of Mes), 2.32, 2.30 (s, 6H each, *o*-CH_3 of Mes). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 331.0 (CTe), 211.6 (RuC(N)$_2$), 139.4 (Ar), 138.6 (Ar), 138.0 (Ar), 137.4 (Ar), 130.1 (Ar), 129.9 (Ar), 93.4 (Cp), 51.9 (CH_2), 21.2 (CH_3), 19.0 (CH_3), 18.6 (CH_3). ^{125}Te{^{1}H} NMR ($CDCl_3$, 95 MHz): δ 937. Anal. Calcd for $C_{27}H_{31}ClN_2RuTe$: C, 50.07; H, 4.82; N, 4.33. Found: C, 50.10; H, 4.50; N, 4.26.

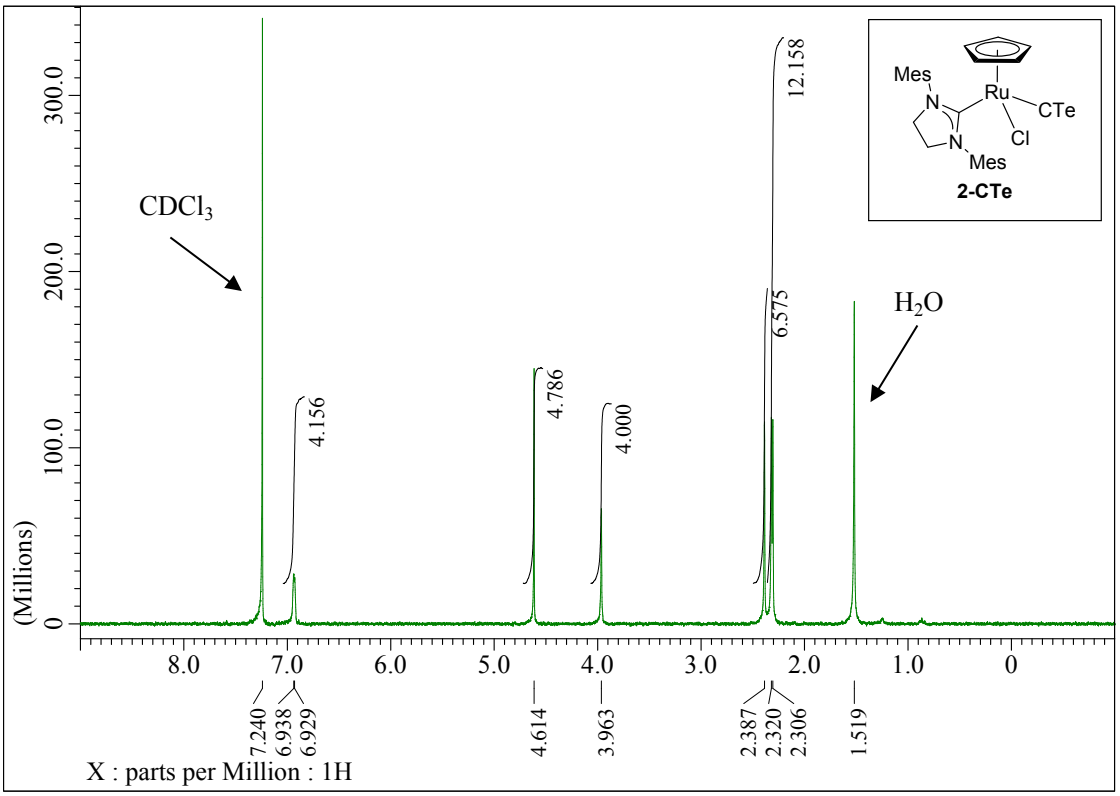


Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2-CTe**.

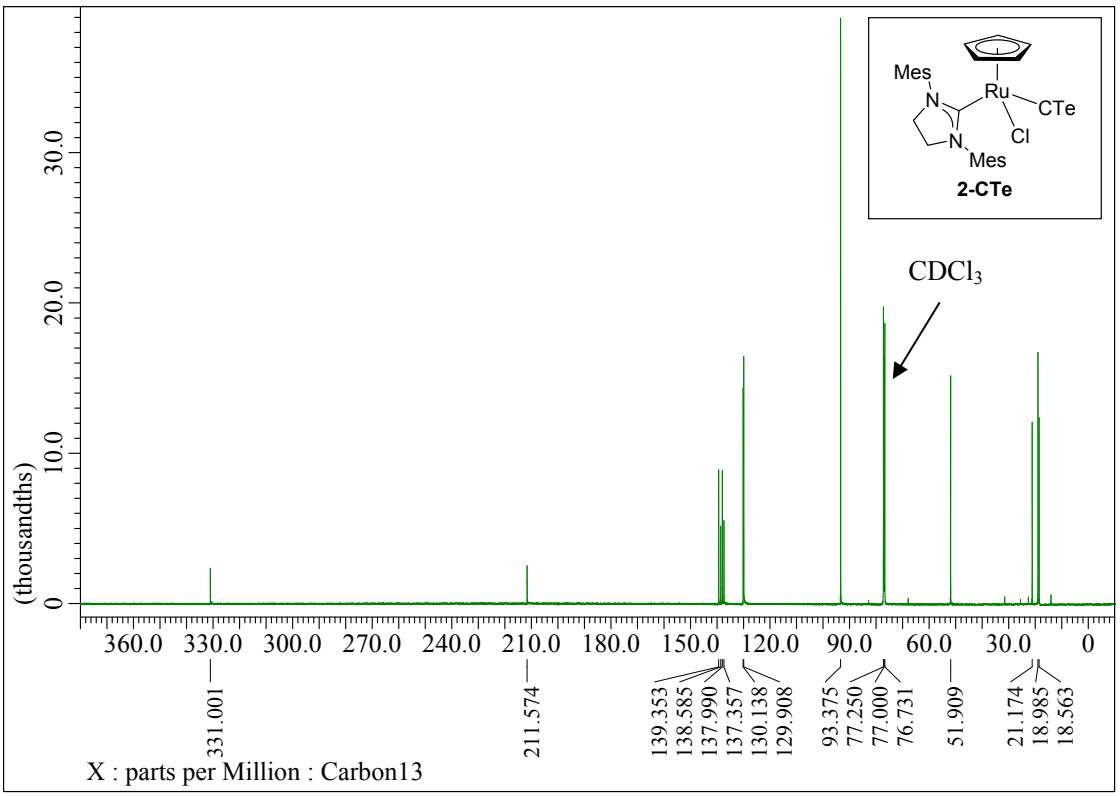


Figure S2. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of **2-CTe**.

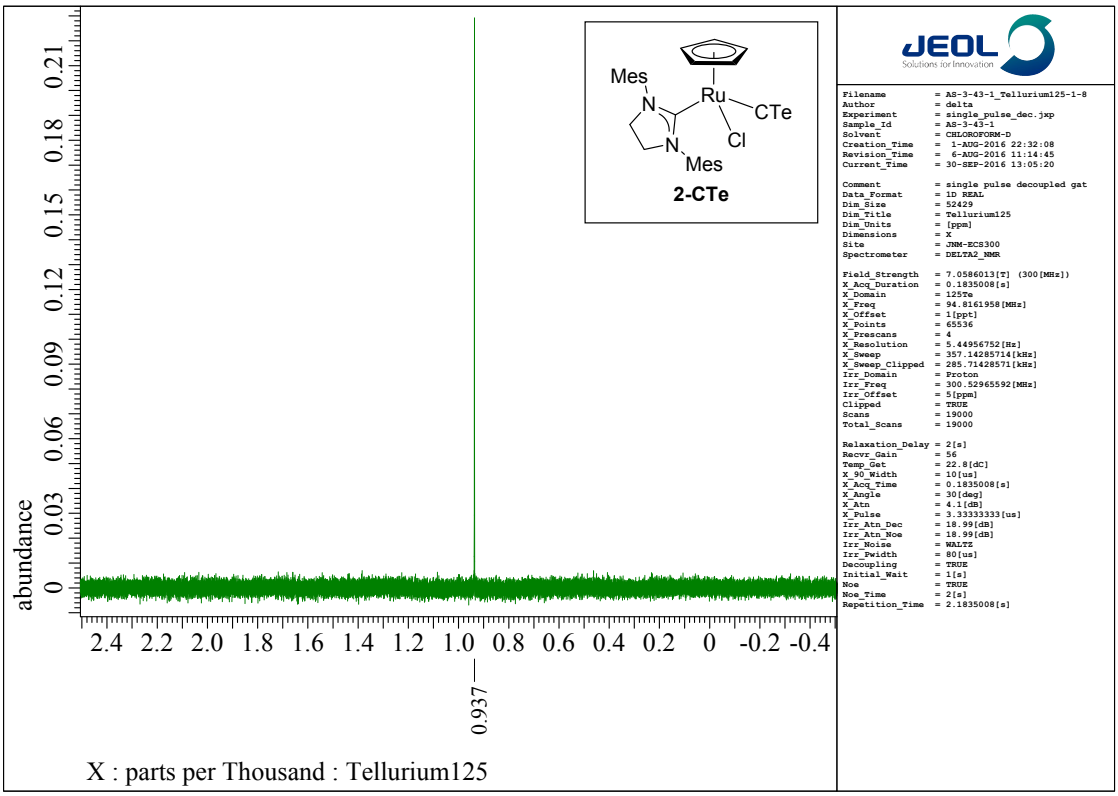


Figure S3. $^{125}Te\{^{1}H\}$ NMR (95 MHz, an offset of 1000 ppm with a spectral window of 3000 ppm, $CDCl_3$) spectrum of **2-CTe**.

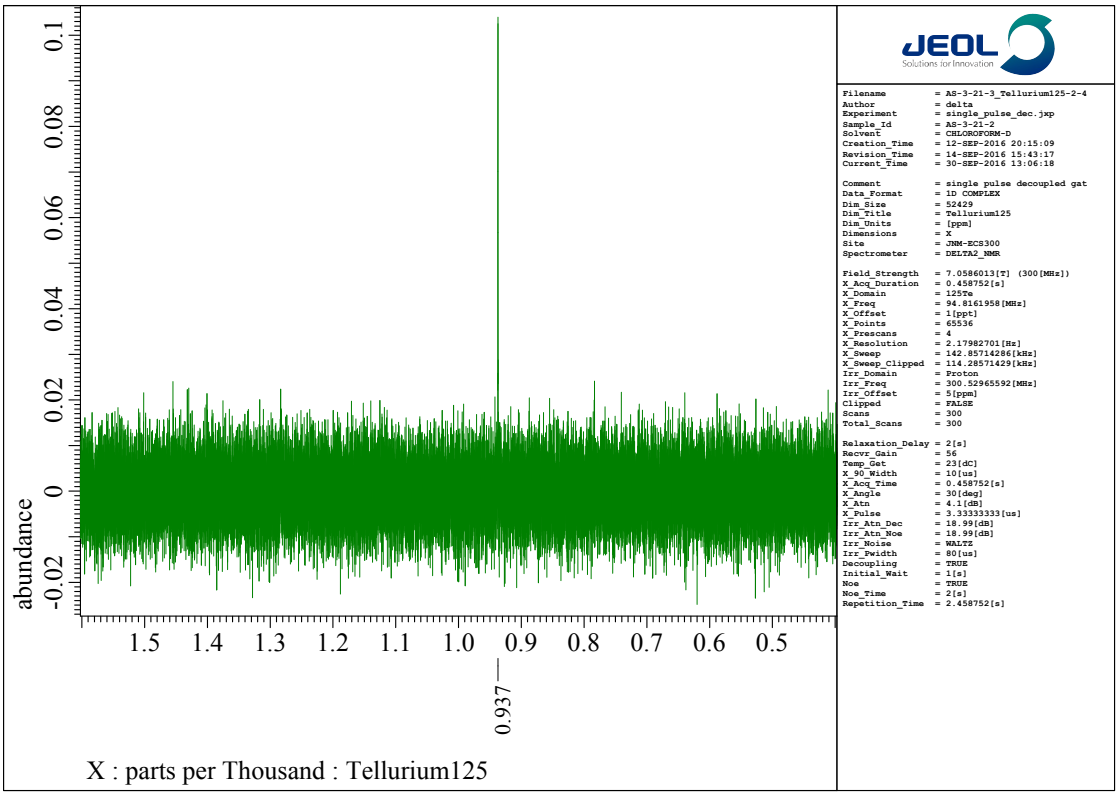


Figure S4. $^{125}Te\{^{1}H\}$ NMR (95 MHz, an offset of 1000 ppm with a spectral window of 1500 ppm, $CDCl_3$) spectrum of **2-CTe**.

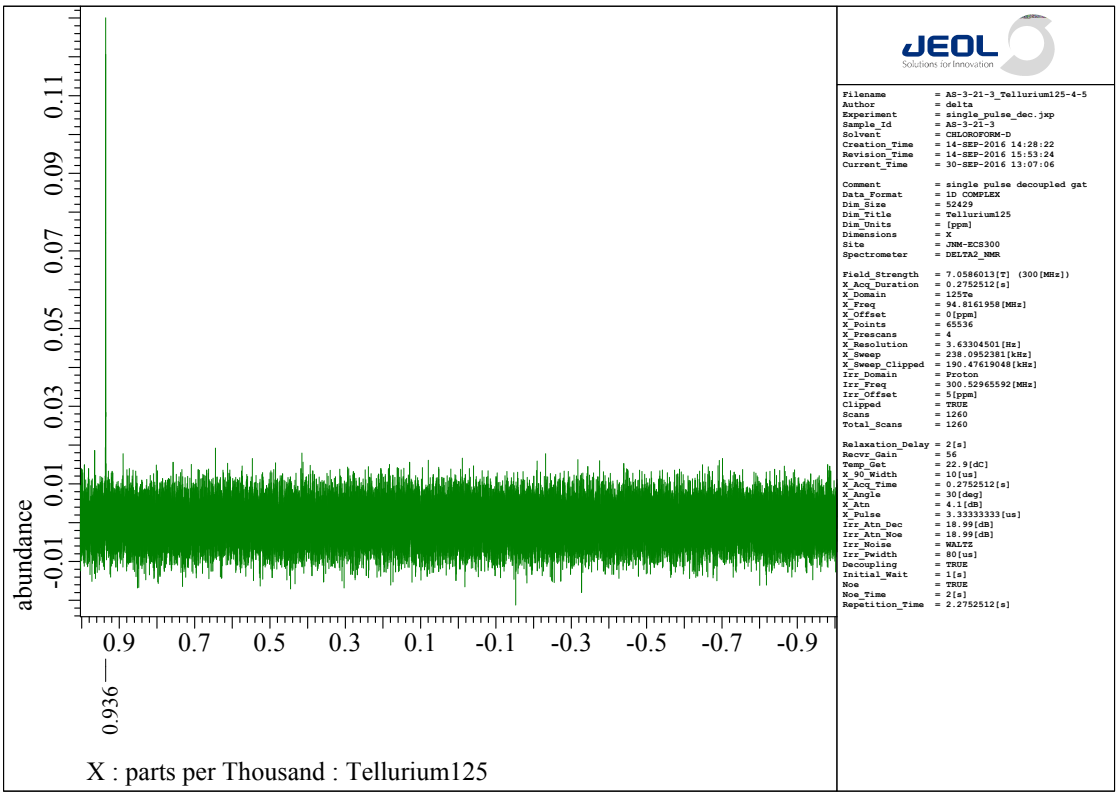
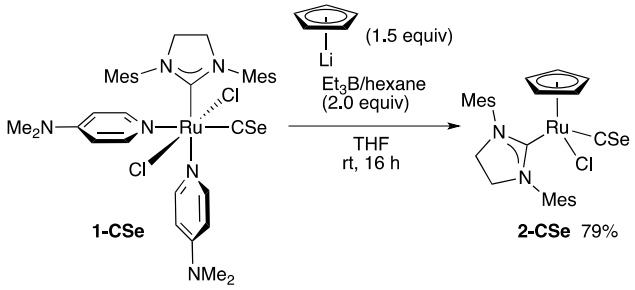


Figure S5. $^{125}Te\{^{1}H\}$ NMR (95 MHz, an offset of 0 ppm with a spectral window of 2000 ppm, $CDCl_3$) spectrum of **2-CTe**.

Synthesis of [CpRuCl(CSe)(H_2IMes)] (**2-CSe**)



To a THF (4.0 mL) solution of CpLi (14 mg, 0.19 mmol, 1.5 equiv) and [$RuCl_2$(CSe)(H_2IMes)(dmap)$_2$] (**1-CSe**, 105.0 mg, 0.13 mmol) was added Et_3B (1.0 M solution in hexane, 0.26 mL, 0.26 mmol, 2.0 equiv) at room temperature, and the mixture was stirred for 16 h at the temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 2/1) and recrystallization (CH_2Cl_2/hexane) to give **2-CSe** (61.2 mg, 0.10 mmol, 79% yield) as orange crystals. IR (cm^{-1}): 1090 (ν_{CSe}). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.94 (s, 4H, Ar of Mes), 4.57 (s, 5H, Cp), 3.96 (s, 4H, N(CH_2)$_2$N), 2.39 (s, 6H, *p*-CH_3 of Mes), 2.31 (s, 12H, *o*-CH_3 of Mes). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 319.5 (CSe), 212.8 (RuC(N)$_2$), 139.1 (Ar), 138.7 (Ar), 138.0 (Ar), 137.5 (Ar), 129.9 (Ar), 129.7 (Ar), 90.9 (Cp), 51.8 (CH_2), 21.1 (CH_3), 19.0 (CH_3), 18.5 (CH_3). Anal. Calcd for $C_{27}H_{31}ClN_2RuSe$: C, 54.14; H, 5.22; N, 4.68. Found: C, 54.16; H, 5.16; N, 4.63.

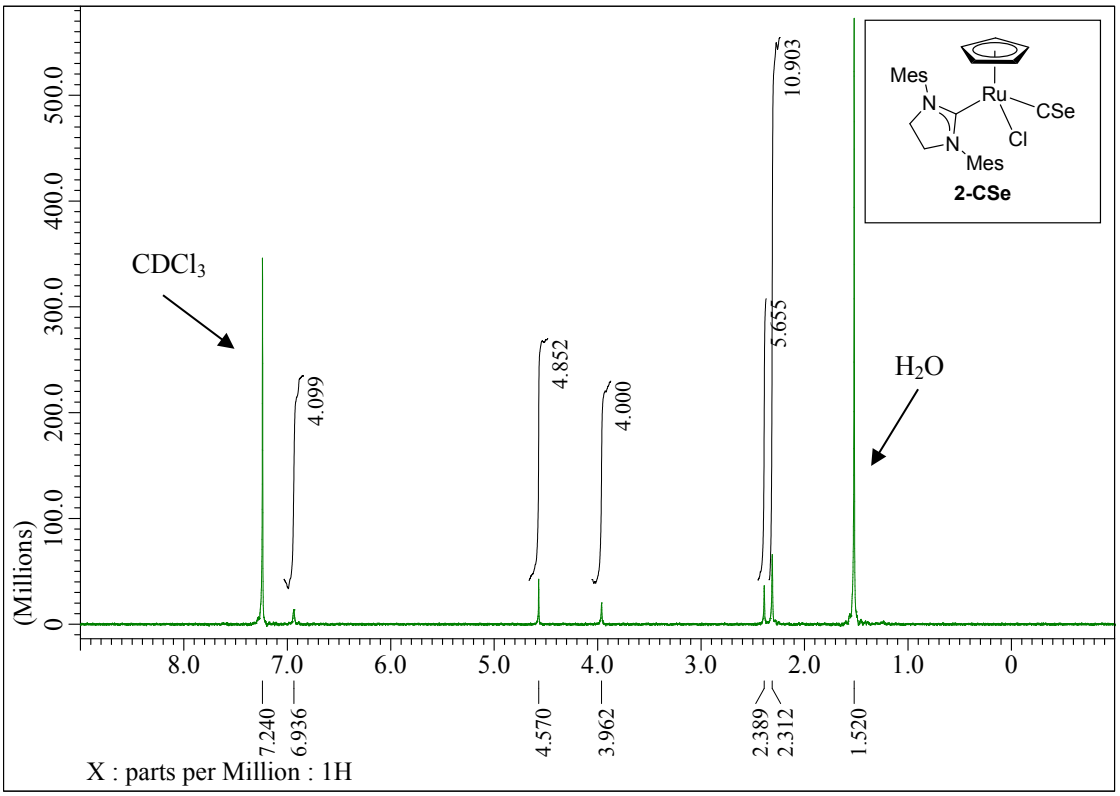


Figure S6. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-CSe**.

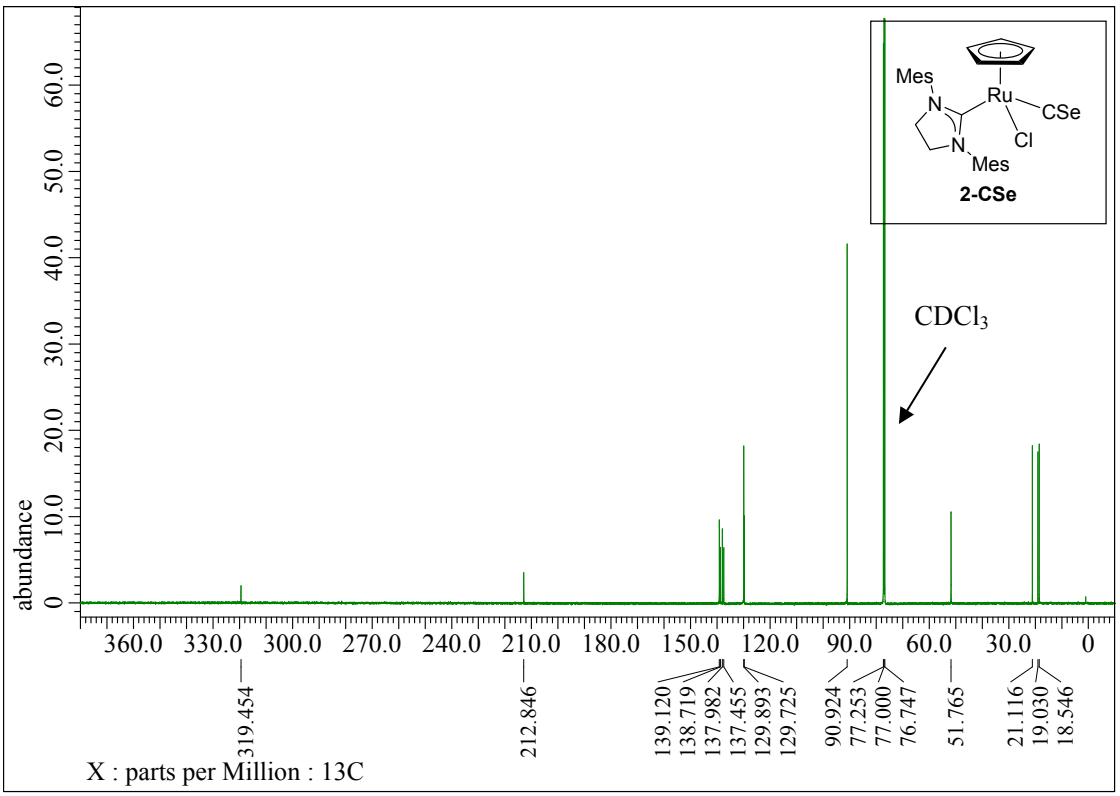
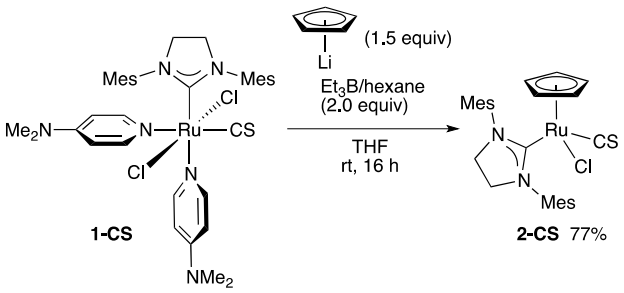


Figure S7. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of **2-CSe**.

Synthesis of [CpRuCl(CS)(H_2IMes)] (**2-CS**)



To a THF (3.2 mL) solution of CpLi (12 mg, 0.17 mmol, 1.5 equiv) and [$RuCl_2$(CS)(H_2IMes)(dmap)$_2$] (**1-CS**, 85.0 mg, 0.11 mmol) was added Et_3B (1.0 M solution in hexane, 0.22 mL, 0.22 mmol, 2.0 equiv) at room temperature, and the mixture was stirred for 16 h at the temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 2/1) and recrystallization (CH_2Cl_2/hexane) to give **2-CS** (47.1 mg, 0.085 mmol, 77% yield) as orange crystals. IR (cm^{-1}): 1232 (ν_{CS}). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.94 (s, 4H, Ar of Mes), 4.52 (s, 5H, Cp), 3.96 (s, 4H, N(CH_2)$_2$N), 2.39 (s, 6H, *p*-CH_3 of Mes), 2.31 (s, 6H each, *o*-CH_3 of Mes). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 300.5 (CS), 213.7 (RuC(N)$_2$), 138.9 (Ar), 138.8 (Ar), 138.0 (Ar), 137.4 (Ar), 129.7 (Ar), 129.6 (Ar), 89.2 (Cp), 51.7 (CH_2), 21.1 (CH_3), 19.0 (CH_3), 18.5 (CH_3). Anal. Calcd for $C_{27}H_{31}ClN_2RuS$: C, 58.73; H, 5.66; N, 5.07. Found: C, 58.67; H, 5.65; N, 5.04.

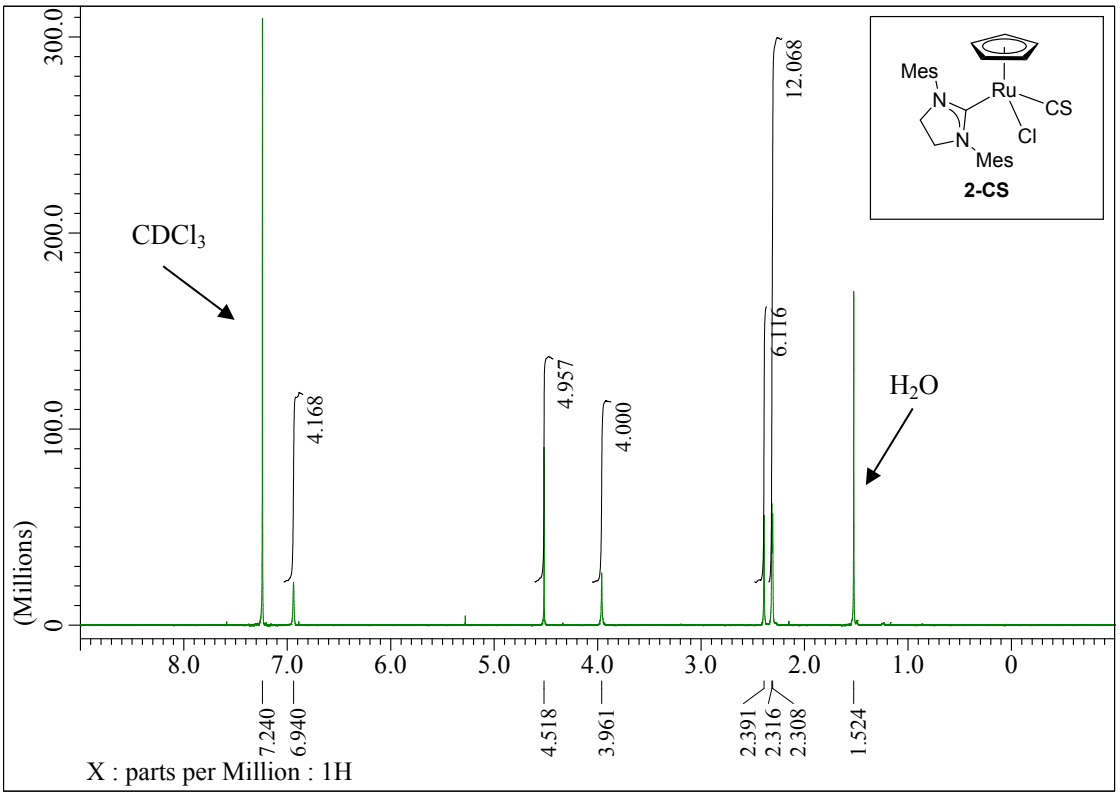


Figure S8. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-CS**.

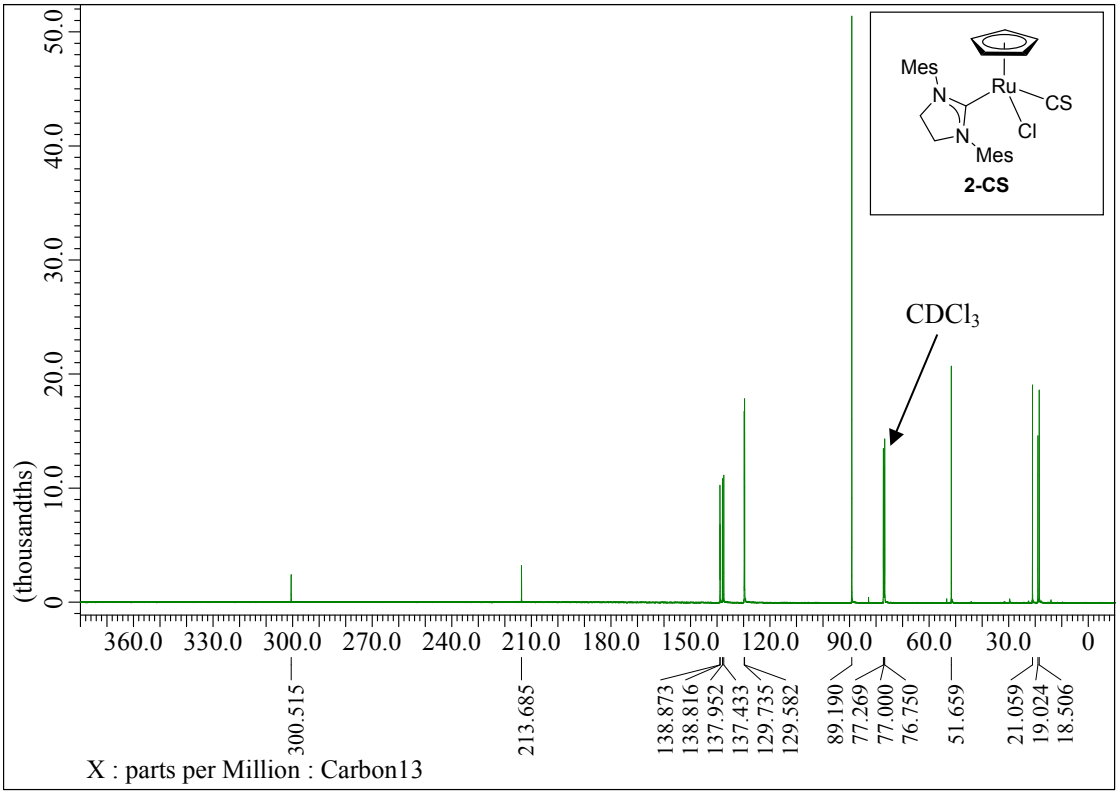
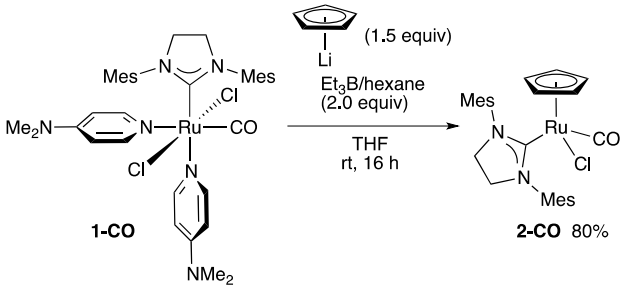


Figure S9. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of **2-CS**.

Synthesis of [CpRuCl(CO)(H_2IMes)] (**2-CO**)



To a THF (2.0 mL) solution of CpLi (7 mg, 0.97 mmol, 1.5 equiv) and [$RuCl_2$(CO)(H_2IMes)(dmap)$_2$] (**1-CO**, 50.0 mg, 0.066 mmol) was added Et_3B (1.0 M solution in hexane, 0.13 mL, 0.13 mmol, 2.0 equiv) at room temperature, and the mixture was stirred for 16 h at the temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 2/1) to give **2-CO** (28.5 mg, 0.053 mmol, 80% yield) as yellow crystals. IR (cm^{-1}): 1933 (ν_{CO}). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.98 (s, 4H, Ar of Mes), 4.34 (s, 5H, Cp), 3.95 (s, 4H, N(CH_2)$_2$N), 2.38 (s, 6H, *p*-CH_3 of Mes), 2.33, 2.31 (s, 6H each, *o*-CH_3 of Mes). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz): δ 214.8 (RuC(N)$_2$), 202.3 (CO), 138.7 (Ar), 138.6 (Ar), 137.7 (Ar), 137.2 (Ar), 129.7 (Ar), 129.5 (Ar), 82.9 (Cp), 51.3 (CH_2), 21.1 (CH_3), 19.0 (CH_3), 18.4 (CH_3). Anal. Calcd for $C_{27}H_{31}ClN_2ORu$: C, 60.49; H, 5.83; N, 5.23. Found: C, 60.35; H, 5.58; N, 5.12.

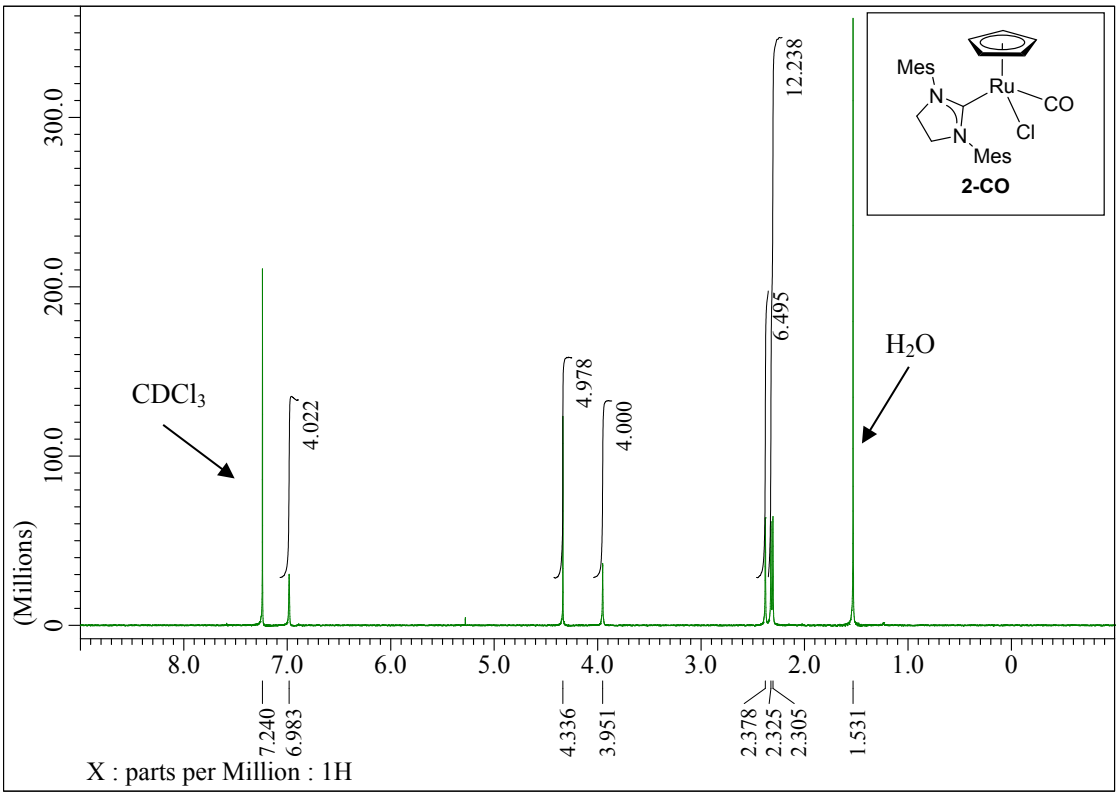


Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2-CO**.

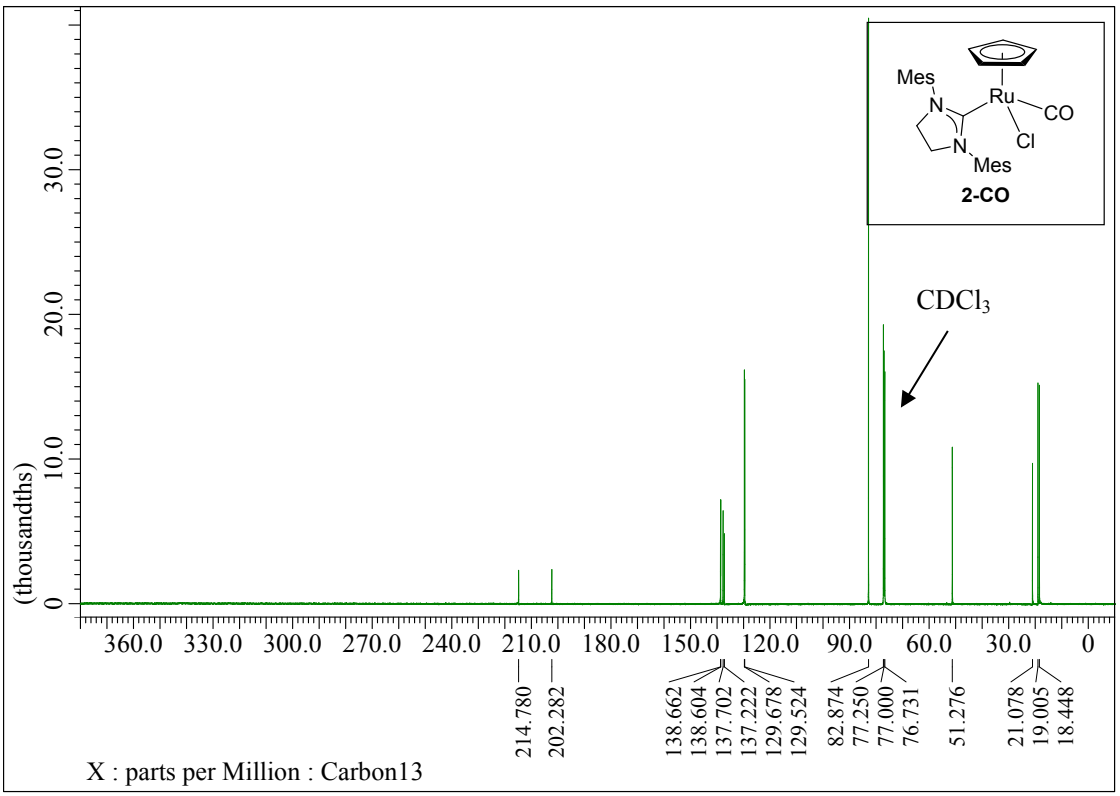


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of **2-CO**.

Reaction of [CpRuCl(CTe)(H_2IMes)] (2-CTe) with PPh_3 (Scheme 4). A mixture of [CpRuCl(CTe)(H_2IMes)] (**2-CTe**, 6.5 mg, 0.01 mmol) and PPh_3 (52.4 mg, 0.20 mmol, 20 equiv) in toluene (1 mL) was stirred at room temperature for 16 h. The $^{31}P\{^1H\}$ NMR analysis of the reaction mixture showed only one signal due to PPh_3 (δ −5.2). The mixture was allowed to warm to 100 °C and stirred for 25 h. The resulting mixture was dried under vacuum to leave orange solids. The ^1H and $^{31}P\{^1H\}$ NMR analysis of the solid indicated that no reaction of **2-CTe** proceeded.

Reaction of 2-CTe with S_8 (Scheme 5). A mixture of [CpRuCl(CTe)(H_2IMes)] (**2-CTe**, 13.0 mg, 0.020 mmol) and S_8 (3.2 mg, 0.012 mmol, 5.0 equiv as S) in CH_2Cl_2 (0.5 mL) was stirred at room temperature for 16 h. The resulting mixture was dried under vacuum. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 2/1) to give **2-CS** (9.3 mg, 0.017 mmol, 84% yield) as yellow crystals. The spectroscopic data were consistent with those described above.

Reaction of 2-CTe with O_2 in the presence of Et_3B·DMAP (Scheme 6). A mixture of [CpRuCl(CTe)(H_2IMes)] (**2-CTe**, 13.0 mg, 0.020 mmol) and Et_3B·DMAP (22.0 mg, 0.100 mmol, 5.0 equiv) in CH_2Cl_2 (13.0 mL) was bubbled with O_2 via a stainless needle for 15 min, and this was stirred at room temperature for 17 h under an atmosphere of oxygen (balloon). The resulting mixture was dried under vacuum. To the residue was added $CDCl_3$ and naphthalene (10.9 mg, 0.085 mmol) as an internal standard. The ^1H NMR analysis of the sample indicated the formation of **2-CO** in 49% NMR yield.

X-ray Diffraction Studies. Diffraction data for **2-CTe** were collected on a Bruker Apex II Ultra X-ray diffractometer equipped with a Mo Kα radiation (λ = 0.71073Å) at −173 °C. Intensity data were processed using Apex2 software suit. The structure solution and refinements were carried out by using the Yadokari-XG[S2] graphical interface. The position of the non-hydrogen atoms were determined by using the SHELXT[S3] program and refined on F^2 by full-matrix least-squares techniques using the SHELXL-2014[S4] program. All the non-hydrogen atoms were refined with anisotropic thermal parameters, while all the hydrogen atoms were placed using AFIX instructions. Details of the diffraction data are summarized in Table S1.

[S2] (a) K. Wakita, *Yadokari-XG, Software for Crystal Structure Analysis*, 2001. (b) C. Kabuto, S. Akine and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218–224.
[S3] G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3–8.
[S4] (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112–122. (b) G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3–8.

Table S1. Crystal data and structure refinement for **2-CTe**

CCDC	1500779	
Identification code	**2-CTe** (AS-2-6)	
Empirical formula	$C_{27}H_{31}ClN_2RuTe$	
Formula weight	647.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group $P2_1/n$		
Unit cell dimensions	a = 13.7432(14) Å	α = 90°.
	b = 14.4994(15) Å	β = 109.4860(10)°.
	c = 13.7674(14) Å	γ = 90°.
Volume	2586.3(5) Å^3	
Z	4	
Density (calculated)	1.663 Mg/m^3	
Absorption coefficient	1.832 mm^{-1}	
F(000)	1280	
Crystal size	0.150 × 0.110 × 0.090 mm^3	
Theta range for data collection	2.106 to 27.499°.	
Index ranges	$-17 \le h \le 17$, $-18 \le k \le 18$, $-17 \le l \le 17$	
Reflections collected	28121	
Independent reflections	5910 [R(int) = 0.0179]	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5910 / 0 / 295	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0166, wR2 = 0.0414	
R indices (all data)	R1 = 0.0181, wR2 = 0.0423	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.542 and −0.360 e.Å^{-3}	

Computational Details. All density functional theory (DFT) calculations were performed using the Gaussian 09 package.[S5] The computers used in the present study are the computer facilities at the Academic Center for Computing Media Studies (ACCMS), Kyoto University, Japan. The geometries of **2-CE** were fully optimized using the M06[S6] density functional with the SDD[S7] basis set. The SDD basis set consists of the Dunning/Hujinaga full double-ζ basis set (D95) for the elements up to Ar and the Stuttgart/Dresden ECPs for the remainder of the periodic table. Vibrational analysis based on force constant matrices (Hessians) was carried out at the stationary points in order to identify them as minima (all positive constants), transition states (one negative force constant), or higher-order saddle points. Wiberg bond index[S8] in the natural atomic orbital (NAO)[S9] basis were evaluated by using the natural population analysis (NPA). Optimized Cartesian coordinates for **2-CE** were summarized in Tables S2 to S5.

[S5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[S6] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

[S7] (a) T. H. Dunning Jr., P. J. Hay, *In Modern Theoretical Chemistry*, H. F. Schaefer III, Ed.; Plenum : New York, 1976, pp. 1–28; (b) D. Andrae, U. Häsußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.

[S8] K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083–1096.

[S9] A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1998, **88**, 899–926.

Table S2. Optimized Cartesian Coordinates for **2-CTe**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.348332	-1.061440	0.213383
2	17	0	0.277581	-0.816505	2.657885
3	52	0	-3.234317	-1.773819	-0.283371
4	6	0	-1.421417	-1.094712	-0.002796
5	7	0	1.786265	1.634605	0.238768
6	6	0	0.135164	3.308308	0.359185
7	1	0	-0.265727	3.810331	1.246222
8	1	0	-0.182598	3.877814	-0.524701
9	7	0	-0.390886	1.924049	0.273947
10	6	0	0.583876	0.972536	0.192269
11	6	0	3.099364	1.119737	-0.016826
12	6	0	3.551989	1.088014	-1.351936
13	6	0	-1.805972	1.809936	0.059439
14	6	0	1.652053	3.098879	0.422264
15	1	0	2.191815	3.630538	-0.370943
16	1	0	2.081087	3.398529	1.385750
17	6	0	-2.685477	1.852894	1.158112
18	6	0	-4.064081	1.900690	0.900858
19	1	0	-4.754421	1.913923	1.743403
20	6	0	2.662554	1.537981	-2.482020
21	1	0	2.509644	2.626568	-2.461030
22	1	0	1.667493	1.079182	-2.422831
23	1	0	3.104392	1.287463	-3.452269
24	6	0	7.122685	-0.208288	-0.856346
25	1	0	7.299837	-0.310856	-1.931747
26	1	0	7.323133	-1.177903	-0.385826
27	1	0	7.859244	0.501849	-0.460895
28	6	0	3.469198	0.810956	2.476443
29	1	0	4.297454	0.642224	3.172277
30	1	0	2.696810	0.050466	2.658154
31	1	0	3.004211	1.773002	2.724356
32	6	0	-4.573386	1.908812	-0.406360
33	6	0	-3.667908	1.884316	-1.480754

34	1	0	-4.048503	1.882951	-2.501764
35	6	0	4.856069	0.638236	-1.610908
36	1	0	5.208558	0.596554	-2.640888
37	6	0	-2.285026	1.831431	-1.268189
38	6	0	-2.179578	1.784912	2.570816
39	1	0	-2.956581	2.085336	3.281258
40	1	0	-1.293067	2.410237	2.731431
41	1	0	-1.865136	0.759078	2.806495
42	6	0	5.717925	0.255822	-0.570835
43	6	0	5.248584	0.334962	0.751748
44	1	0	5.910851	0.053513	1.569980
45	6	0	3.947467	0.766336	1.052632
46	6	0	-6.058096	1.894599	-0.655995
47	1	0	-6.407077	0.863307	-0.802048
48	1	0	-6.321930	2.460605	-1.556396
49	1	0	-6.612604	2.313345	0.190515
50	6	0	-1.343549	1.728369	-2.438152
51	1	0	-1.847303	1.996967	-3.372332
52	1	0	-0.981237	0.693528	-2.534633
53	1	0	-0.459370	2.371023	-2.325541
54	6	0	2.482814	-2.041990	-0.244887
55	1	0	3.430695	-1.611054	0.043575
56	6	0	1.715790	-2.972810	0.519206
57	1	0	1.950136	-3.310448	1.519130
58	6	0	0.541007	-3.332052	-0.220473
59	1	0	-0.235364	-4.012726	0.098060
60	6	0	0.567480	-2.592119	-1.454213
61	1	0	-0.178361	-2.640804	-2.236119
62	6	0	1.756789	-1.778371	-1.459726
63	1	0	2.087405	-1.146899	-2.272572

Table S3. Optimized Cartesian Coordinates for **2-CSe**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.219770	1.159675	0.156708
2	17	0	-0.131512	1.009369	2.612003
3	6	0	1.557371	1.307917	-0.050437
4	7	0	-1.462333	-1.628028	0.264723
5	6	0	0.300235	-3.177902	0.462211
6	1	0	0.685424	-3.594914	1.399365
7	1	0	0.705813	-3.774771	-0.364955
8	7	0	0.728234	-1.766127	0.313620
9	6	0	-0.308446	-0.883733	0.205117
10	6	0	-2.809149	-1.202406	0.023339
11	6	0	-3.288333	-1.212573	-1.303378
12	6	0	2.128091	-1.555875	0.075660
13	6	0	-1.229688	-3.080568	0.437656
14	1	0	-1.679272	-3.636718	-0.395257
15	1	0	-1.693512	-3.428728	1.367743
16	6	0	3.025220	-1.486617	1.157982
17	6	0	4.397060	-1.408224	0.872828
18	1	0	5.101342	-1.332339	1.700497
19	6	0	-2.402999	-1.629068	-2.450152
20	1	0	-2.290724	-2.721871	-2.490096
21	1	0	-1.393845	-1.207492	-2.363617
22	1	0	-2.831230	-1.312595	-3.407692
23	6	0	-6.915404	-0.109398	-0.755676
24	1	0	-7.073719	0.142262	-1.809423
25	1	0	-7.219263	0.751730	-0.150019
26	1	0	-7.591026	-0.937181	-0.506265
27	6	0	-3.149076	-0.874714	2.518370
28	1	0	-3.979371	-0.852223	3.231751
29	1	0	-2.505576	-0.002117	2.698231
30	1	0	-2.523353	-1.748357	2.736343
31	6	0	4.881374	-1.403435	-0.443942
32	6	0	3.960338	-1.502130	-1.500321
33	1	0	4.321122	-1.498439	-2.528493

34	6	0	-4.618781	-0.834699	-1.541328
35	1	0	-4.991405	-0.820506	-2.565120
36	6	0	2.583005	-1.576162	-1.259779
37	6	0	2.540337	-1.425786	2.578706
38	1	0	3.364740	-1.587291	3.280918
39	1	0	1.753530	-2.160184	2.789457
40	1	0	2.094516	-0.442928	2.781713
41	6	0	-5.481373	-0.487023	-0.489129
42	6	0	-4.984240	-0.525519	0.824425
43	1	0	-5.643561	-0.267682	1.652678
44	6	0	-3.655618	-0.882099	1.104176
45	6	0	6.353543	-1.252373	-0.722685
46	1	0	6.602461	-0.194683	-0.882079
47	1	0	6.651868	-1.799241	-1.624080
48	1	0	6.960775	-1.610591	0.115444
49	6	0	1.608405	-1.612234	-2.406548
50	1	0	2.121676	-1.809712	-3.353163
51	1	0	1.094474	-0.642739	-2.492651
52	1	0	0.830012	-2.376994	-2.270733
53	6	0	-2.403637	1.951469	-0.366040
54	1	0	-3.323479	1.459376	-0.082938
55	6	0	-1.723538	2.965659	0.375220
56	1	0	-2.001110	3.319205	1.358441
57	6	0	-0.565649	3.386965	-0.357838
58	1	0	0.149081	4.138005	-0.053954
59	6	0	-0.513408	2.602704	-1.565047
60	1	0	0.239176	2.682096	-2.337842
61	6	0	-1.638013	1.702758	-1.560614
62	1	0	-1.901927	1.017116	-2.353191
63	34	0	3.150731	1.972206	-0.341332

Table S4. Optimized Cartesian Coordinates for **2-CS**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.104593	1.273048	0.090101
2	17	0	0.035181	1.172741	2.544933
3	6	0	1.661565	1.530879	-0.143847
4	7	0	-1.148978	-1.600914	0.205416
5	6	0	0.722503	-3.015592	0.407555
6	1	0	1.115612	-3.391670	1.358843
7	1	0	1.191240	-3.589483	-0.401832
8	7	0	1.045388	-1.577409	0.252663
9	6	0	-0.053040	-0.772344	0.150478
10	6	0	-2.529736	-1.263132	0.025265
11	6	0	-3.069173	-1.276051	-1.277232
12	6	0	2.429098	-1.257496	0.045533
13	6	0	-0.809936	-3.034839	0.346047
14	1	0	-1.194231	-3.598420	-0.514361
15	1	0	-1.268492	-3.444841	1.253444
16	6	0	3.295284	-1.106909	1.145499
17	6	0	4.662407	-0.921619	0.885975
18	1	0	5.341382	-0.786512	1.727138
19	6	0	-2.227889	-1.632483	-2.476455
20	1	0	-2.146760	-2.722223	-2.592036
21	1	0	-1.208052	-1.237499	-2.397964
22	1	0	-2.679000	-1.246005	-3.397606
23	6	0	-6.719731	-0.374499	-0.539146
24	1	0	-6.946684	-0.139175	-1.584036
25	1	0	-7.028969	0.477439	0.076911
26	1	0	-7.342488	-1.229402	-0.247223
27	6	0	-2.776736	-1.059431	2.543319
28	1	0	-3.559184	-0.885648	3.289084
29	1	0	-1.991872	-0.301896	2.676473
30	1	0	-2.312586	-2.030342	2.762281
31	6	0	5.171919	-0.882535	-0.420539
32	6	0	4.282403	-1.052817	-1.494699
33	1	0	4.661894	-1.020944	-2.515599

34	6	0	-4.428832	-0.966571	-1.445005
35	1	0	-4.849045	-0.953369	-2.450276
36	6	0	2.911577	-1.237076	-1.280563
37	6	0	2.785188	-1.067748	2.559096
38	1	0	3.602683	-1.212713	3.273182
39	1	0	2.012677	-1.821206	2.753542
40	1	0	2.309994	-0.096830	2.761242
41	6	0	-5.257694	-0.684610	-0.348486
42	6	0	-4.699257	-0.725415	0.941000
43	1	0	-5.333045	-0.522301	1.803607
44	6	0	-3.343952	-1.020211	1.152063
45	6	0	6.635081	-0.626537	-0.669701
46	1	0	6.813463	0.444821	-0.829065
47	1	0	6.989895	-1.154587	-1.561822
48	1	0	7.248402	-0.938803	0.182316
49	6	0	1.964272	-1.343447	-2.445535
50	1	0	2.507814	-1.505136	-3.381901
51	1	0	1.384411	-0.412740	-2.542747
52	1	0	1.238483	-2.159841	-2.321649
53	6	0	-2.332459	1.924604	-0.374811
54	1	0	-3.211332	1.388125	-0.045750
55	6	0	-1.684370	2.995306	0.318513
56	1	0	-1.945731	3.355382	1.303639
57	6	0	-0.579832	3.461132	-0.465231
58	1	0	0.102046	4.257742	-0.205455
59	6	0	-0.524778	2.648981	-1.655711
60	1	0	0.194303	2.750760	-2.457144
61	6	0	-1.601069	1.694617	-1.593466
62	1	0	-1.851191	0.974638	-2.358974
63	16	0	3.099164	2.215331	-0.449412

Table S5. Optimized Cartesian Coordinates for **2-CO**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.016923	1.342953	0.039147
2	17	0	0.201707	1.226081	2.504398
3	6	0	1.811888	1.595230	-0.117544
4	7	0	-1.033966	-1.547356	0.144346
5	6	0	0.842987	-2.920093	0.476768
6	1	0	1.105968	-3.173444	1.511233
7	1	0	1.415304	-3.567921	-0.196460
8	7	0	1.158246	-1.499756	0.206063
9	6	0	0.050294	-0.700767	0.092434
10	6	0	-2.425572	-1.233111	0.015909
11	6	0	-3.026810	-1.285639	-1.258064
12	6	0	2.530434	-1.144607	-0.002939
13	6	0	-0.668392	-2.979240	0.234695
14	1	0	-0.926721	-3.495847	-0.700579
15	1	0	-1.216350	-3.458413	1.053264
16	6	0	3.404337	-1.018046	1.093843
17	6	0	4.749694	-0.715308	0.833230
18	1	0	5.429795	-0.586930	1.674646
19	6	0	-2.235981	-1.642767	-2.491307
20	1	0	-2.190416	-2.732133	-2.627215
21	1	0	-1.203670	-1.276988	-2.438563
22	1	0	-2.706304	-1.227488	-3.390186
23	6	0	-6.660471	-0.458217	-0.358461
24	1	0	-6.984551	-0.463608	-1.404083
25	1	0	-6.915413	0.518509	0.069546
26	1	0	-7.248246	-1.211063	0.180683
27	6	0	-2.563574	-0.973238	2.540008
28	1	0	-3.324552	-1.064852	3.322119
29	1	0	-1.999312	-0.044653	2.704684
30	1	0	-1.833461	-1.783202	2.663520
31	6	0	5.236480	-0.562912	-0.472979
32	6	0	4.348099	-0.743453	-1.546339
33	1	0	4.714684	-0.641547	-2.567537

34	6	0	-4.401877	-1.018078	-1.365143
35	1	0	-4.869865	-1.038996	-2.348915
36	6	0	2.995752	-1.032662	-1.331648
37	6	0	2.926064	-1.199628	2.508774
38	1	0	3.604942	-0.706633	3.211745
39	1	0	2.888468	-2.264506	2.780560
40	1	0	1.926855	-0.771088	2.649111
41	6	0	-5.184597	-0.736204	-0.235756
42	6	0	-4.564338	-0.737334	1.025892
43	1	0	-5.162711	-0.539591	1.914940
44	6	0	-3.192587	-0.988390	1.175902
45	6	0	6.674528	-0.190307	-0.721844
46	1	0	6.776454	0.897261	-0.826365
47	1	0	7.053890	-0.645496	-1.643675
48	1	0	7.319356	-0.502734	0.106555
49	6	0	2.048195	-1.183675	-2.491687
50	1	0	2.592615	-1.241847	-3.439713
51	1	0	1.362193	-0.324713	-2.540061
52	1	0	1.425153	-2.084265	-2.393820
53	6	0	-2.215470	1.954824	-0.325975
54	1	0	-3.079625	1.441929	0.071864
55	6	0	-1.535450	3.066929	0.281970
56	1	0	-1.741805	3.465265	1.265295
57	6	0	-0.485625	3.501345	-0.581537
58	1	0	0.197267	4.318146	-0.399855
59	6	0	-0.488724	2.629972	-1.739999
60	1	0	0.167860	2.708512	-2.595082
61	6	0	-1.564707	1.689337	-1.583012
62	1	0	-1.854890	0.934823	-2.299371
63	8	0	2.911908	2.014528	-0.256193
