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Spodium Bonding in Bis(alkynyl)mecurials

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General

Experimental work was performed using standard Schlenk techniques using dried and pre-purified nitrogen or in an inert atmosphere glovebox charged with an argon atmosphere unless specified otherwise. Reactions employed dried and degassed solvents distilled over sodium and benzophenone (ethers, arenes and paraffins) or calcium hydride (CH_2Cl_2, MeCN). The compounds $[W(\equiv CSeC\equiv CSiMe_3)(CO)_2(Tp^*)]$[1] has been described previously. All other reagents were used as received from commercial suppliers.

NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1 MHz, $^{13}C\{^1H\}$ at 100.6 MHz, $^{31}P\{^1H\}$ at 162.0 MHz, 19F{1H} at 376.5 MHz), a Bruker Avance 600 (^{1}H at 600.0 MHz, $^{13}C\{^1H\}$ at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.0 MHz, $^{13}C\{^1H\}$ at 176.1 MHz, $^{31}P\{^1H\}$ at 283.4 MHz) spectrometers at the temperatures indicated. Chemical shifts (δ) are reported in ppm with coupling constants given in Hz and are referenced to the solvent resonance or external references ($HgPh_2$ for $^{199}Hg\{^1H\}$, δ_{Hg} = –750 in $CDCl_3$). The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet), br (broad) and combinations thereof for more highly coupled systems. Where applicable, the stated multiplicity refers to that of the primary resonance exclusive of ^{183}W satellites. In select cases, distinct peaks were observed in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra, but to the level of accuracy that is reportable (i.e., two decimal places for ^{1}H NMR, one decimal place for $^{13}C\{^1H\}$ NMR) they are reported as having the same chemical shift.

The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. The B*H* protons give rise to very broad signals around 4–5 ppm in the ^{1}H NMR spectra due to coupling to the quadrupolar boron nuclei. These are generally not listed in the experimental NMR data as their chemical shifts and associated integrals are not determined accurately. The BH unit, being remote from the metal centre of interest is not particularly responsive to variations and accordingly $^{11}B\{^1H\}$ NMR spectra were not recorded.

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer (liquid) or Perkin Elmer FTIR Spectrum Two (solid state ATR, diamond anvil). Signals are denoted according to their absorption strength such as very sharp (vs), strong (s), medium (m), weak (w) or broad (br). Elemental microanalytical data were provided by Macquarie University, Australia, with the caveat that compounds containing B–N bonds are considered prone to incomplete oxidation in the combustion analysis (formation of refractory boron nitride materials). Solvates evident from data were confirmed where possible by NMR spectroscopy. High and low resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or dichloromethane as the matrix.

Crystallographic Details

Data for X-ray crystallography were collected with Agilent Technologies Xcalibur or Supernova/EosS2-CCD diffractometers as indicated using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) employing the CrysAlis PRO-CCD and -RED software,[2] with Gaussian absorption corrections being applied. The structures were solved using intrinsic phasing and refined by full-matrix least-squares on F^2 in an anisotropic (for non-hydrogen atoms) approximation using the SHELXS or SHELXT and SHELXL programs,[3,4] implemented within the Olex2 suite of programs.[5] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[6,7]

Computational Details

Computational studies were performed by using the *SPARTAN20*® suite of programs.[8] Geometry optimisation (gas phase) for diatomics and metal complexes was performed at the

DFT level of theory using the exchange functionals ωB97X-D of Head-Gordon.[9,10] The Los Alamos effective core potential type basis set (LANL2Dζ) of Hay and Wadt [11-12] was used for W and Hg while Pople basis sets[15] were used for all other atoms. Frequency calculations were performed for all compounds to confirm that each optimized structure was a local minimum and also to identify vibrational modes of interest. Cartesian atomic coordinates and thermodynamic properties are provided below.

Synthetic Procedures and Crystallographic Data

Synthesis of [{(Tp*)(CO)$_2$W(≡CSeC≡C)}$_2$Hg] (3). To a flask containing **1a** (0.500 g, 0.69 mmol) and $HgCl_2$ (0.095 g, 0.35 mmol) was added CH_2Cl_2 (5 mL) and [NBu_4]F (1.0 M in THF, 1.30 mL, 1.30 mmol). The resulting bright orange solution was allowed to stir for 12 hours. Volatiles were removed under reduced pressure and the crude residue was taken up in minimum dichloromethane before loading onto a silica gel chromatography column. Eluting firstly with 3:1 petrol/dichloromethane yielded a pale yellow band, corresponding to [W(≡CCl)(CO)$_2$(Tp*)]. The intended product was then eluted with 1:1 petrol/dichloromethane mixture as a bright orange band which was collected, and volatiles were removed under reduced pressure to yield pure **3** as an orange solid (0.402 g, 0.27 mmol, 77%).

IR (CH_2Cl_2, ν/cm^{-1}): 1988s, 1897s ν_{CO}. 2092 $\nu_{C\equiv C}$. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ_H = 2.32 (s, 6 H, pzC*H*$_3$), 2.36 (s, 12 H, pzC*H*$_3$), 2.41 (s, 6 H, pzC*H*$_3$), 2.56 (s, 12 H, pzC*H*$_3$), 5.77 (s, 2 H, pz*H*), 5.91 (s, 4 H, pz*H*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ_C = 12.9, 13.0, 15.7, 17.1 (pz*C*H$_3$), 79.8 (Se*C*≡C, $^1J_{SeC}$ 204 Hz), 106.9, 107.2 (pz*C*H), 137.2 (SeC≡*C*, $^1J_{HgC}$ = 2473 Hz), 144.8, 145.7, 152.5, 153.0 (pz*C*^{3,5}CH$_3$), 223.2 (*C*O, $^1J_{WC}$ = 164.6 Hz), 233.5 (W≡*C*, $^1J_{WC}$ = 227.3 Hz). ^{77}Se{^{1}H} NMR (76 MHz, $CDCl_3$, 298 K): δ_{Se} = 510. ^{199}Hg{^{1}H} NMR (72 MHz, $CDCl_3$, 298 K): δ_{Hg} = –963 (*cf.* δ_{Hg} = –972 for Hg(C≡CC_6H_4Me-4)$_2$). MS (ESI, *m/z*): Found: 1531.0775. Calc. for $C_{40}H_{44}{}^{11}B_2{}^{202}HgN_{12}O_4{}^{80}Se_2{}^{184}W_2Na$ [M+Na]$^+$: 1531.0797. Anal. Found: C, 31.78; H, 2.83; N, 11.04%. Calc. for $C_{40}H_{44}B_2HgN_{12}O_4Se_2W_2$: C, 31.93; H, 2.95; N, 11.17%.

Single crystals of the phenanthroline adduct of **3.phen** suitable for X-ray diffractometry were grown by vapour diffusion of a saturated solution in CH_2Cl_2 containing phenanthroline into *n*-pentane. *Crystal data for* $C_{52}H_{52}B_2HgN_{14}O_4Se_2W_2$ (**3.phen**: M_w = 1684.90 g.mol^{-1}): triclinic, space group *P*-1 (no. 2), *a* = 13.7335(9) Å, *b*= 21.8752(11) Å, *c*= 22.6730(13) Å, *α* = 117.984(6)°, *β* = 91.487(5)°, γ = 103.840(5)°, *V* = 5764.1(7) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(Cu Kα) = 13.798 mm^{-i}, D_{calc} = 1.942 Mg.m^{-3}, 34266 reflections measured (7.446° ≤ 2Θ ≤ 141.936°), 21405 unique (R_{int} = 0.0660, R_{sigma} = 0.1216) which were used in all calculations. The final R_1 was 0.0704 ($I > 2\sigma(I)$) and wR_2 was 0.1949 (all data) for 1411 refined parameters without restraints. A solvent mask was calculated for the highly volatile pentane solvent and 27 electrons were found in a volume of 147 Å^3 in 2 voids per unit cell. This is consistent with the presence of $^1/_6$ of a C_5H_{12} solvate per asymmetric unit which accounts for 28 electrons per unit cell. CCDC 2033004.

If rather than subjecting the crude reaction mixture to chromatographic purification, hexane vapour is allowed to diffuse into the mixture, poor quality crystals of the TBAF adduct [^{n}Bu$_4$N][**3.F**] were obtained. Crystallographic analysis confirmed the connectivity, however due to the low quality of the data set the poor precision of the structural model precludes detailed geometrical analysis. For this reason, the Crystallographic Information File (.cif) is provided in the accompanying file but has *not* been deposited with the CCDC.

Crystal data for $C_{56}H_{80}B_2FHgN_{13}O_4Se_2W_2$ ([^{n}Bu$_4$N][**3.F**]: M_w = 1766.16 g.mol^{-1}): orthorhombic, space group *P*bca (no. 16), *a* = 15.7048(4) Å, *b* = 27.7070(7) Å, *c*= 35.3368(19) Å, *V* = 15376.2(10) Å^3, *Z* = 8, *T* = 150.0(1) K, μ(Cu Kα) = 13.798 mm^{-i}, orange late 0.20 x 0.12 x 0.02 mm, D_{calc} = 1.526 Mg.m^{-3}, 23413 reflections measured (6.380° ≤ 2Θ ≤ 135.368°), 5360 unique which were used in all calculations. The final R_1 was 0.1264 ($I > 2\sigma(I)$) and wR_2 was 0.3288 (all data) for 639 refined parameters with 719 restraints. The asymmetric unit contains one equivalent of [^{n}Bu$_4$N][**3.F**] in addition to other unknwon solvates for which no sensible disordered model could be developed. The SQUEEZE routine within PLATON was used to account for the electron density, identifying 3287 Å^3 and 577.2 electrons per unit cell. The formulae weight, density etc. provided do not include any correction for the unidentified solvate.

Structural characterisation of [W(≡CSeC≡CH)(CO)$_2${(Tp*)] (1b). At the time of publishing,1a structural data were not available for complex **1b**. In the interim these have been acquired and provided here.

Single crystals suitable for X-ray diffractometry were grown by slow evaporation of a CH_2Cl_2/ethanol/hexane mixture. *Crystal data for* $C_{20}H_{23}BN_6O_2SeW$ (M_w = 653.06 g.mol^{-1}): monoclinic, space group $P2_1/c$ (no. 14), *a* = 7.9715(3) Å, *b* = 18.2689(6) Å, *c* = 19.7379(8) Å, *β* = 101.415(3)°, *V* = 2817.58(18) Å^3, *Z* = 4, *T* = 150.0(1) K, μ(Cu Kα) = 9.270 mm^{-1}, D_{calc} = 1.540 Mg.m^{-3}, 8595 reflections measured (9.142° ≤ 2Θ ≤ 133.194°), 4934 unique (R_{int} = 0.0343, R_{sigma} = 0.0691) which were used in all calculations. The final R_1 was 0.0981 ($I > 2\sigma(I)$) and wR_2 was 0.2139 (all data) for 290 refined parameters with 23 restraints. A solvent mask was calculated and 198 electrons were found in a volume of 626 Å^3 in 1 void per unit cell. This is consistent with the presence of one C_6H_{14} solvate per asymmetric unit which accounts for 200 electrons per unit cell. CCDC 2033047.

Notes and references

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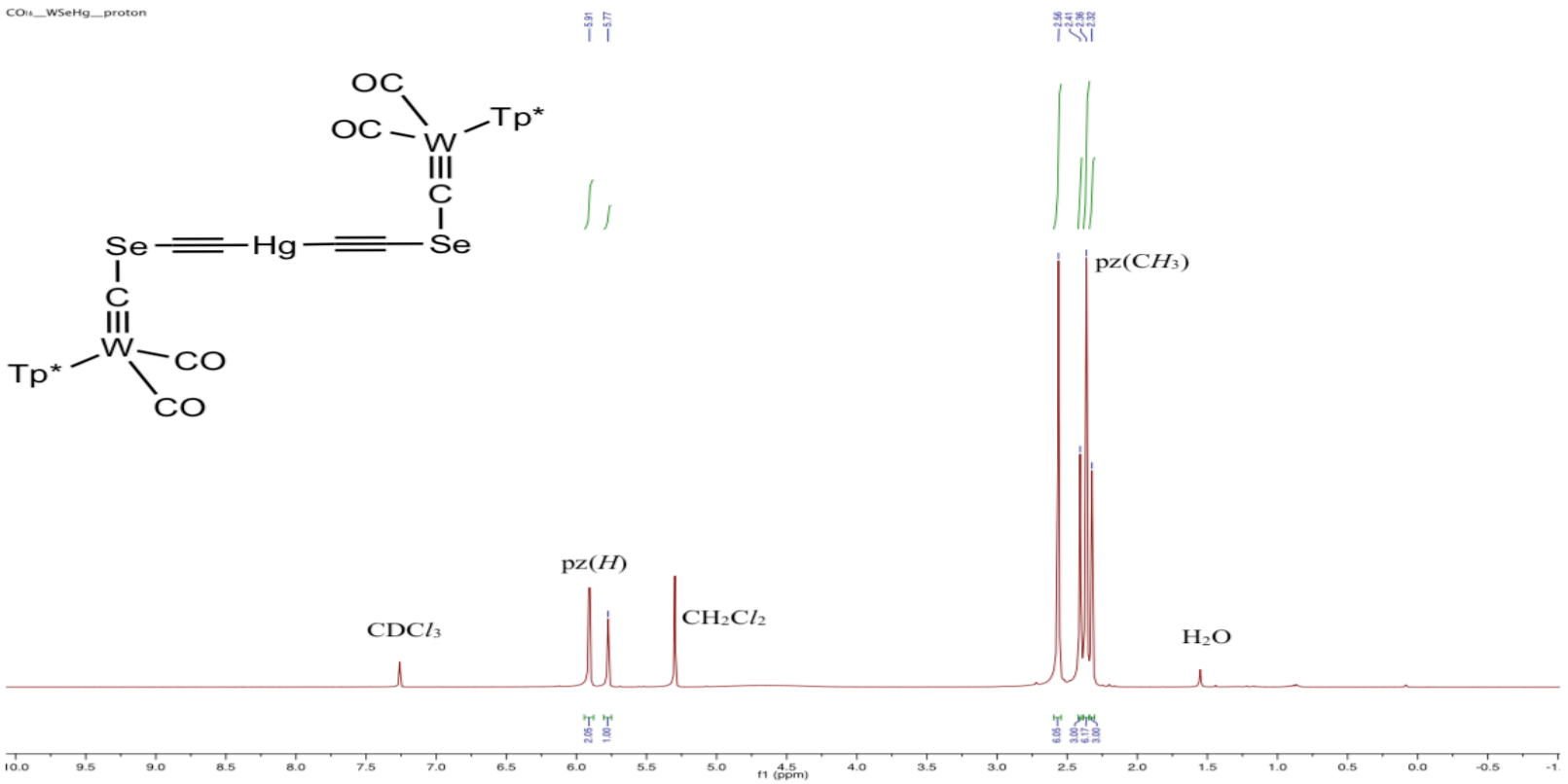

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C, δ) of Compound **3**.

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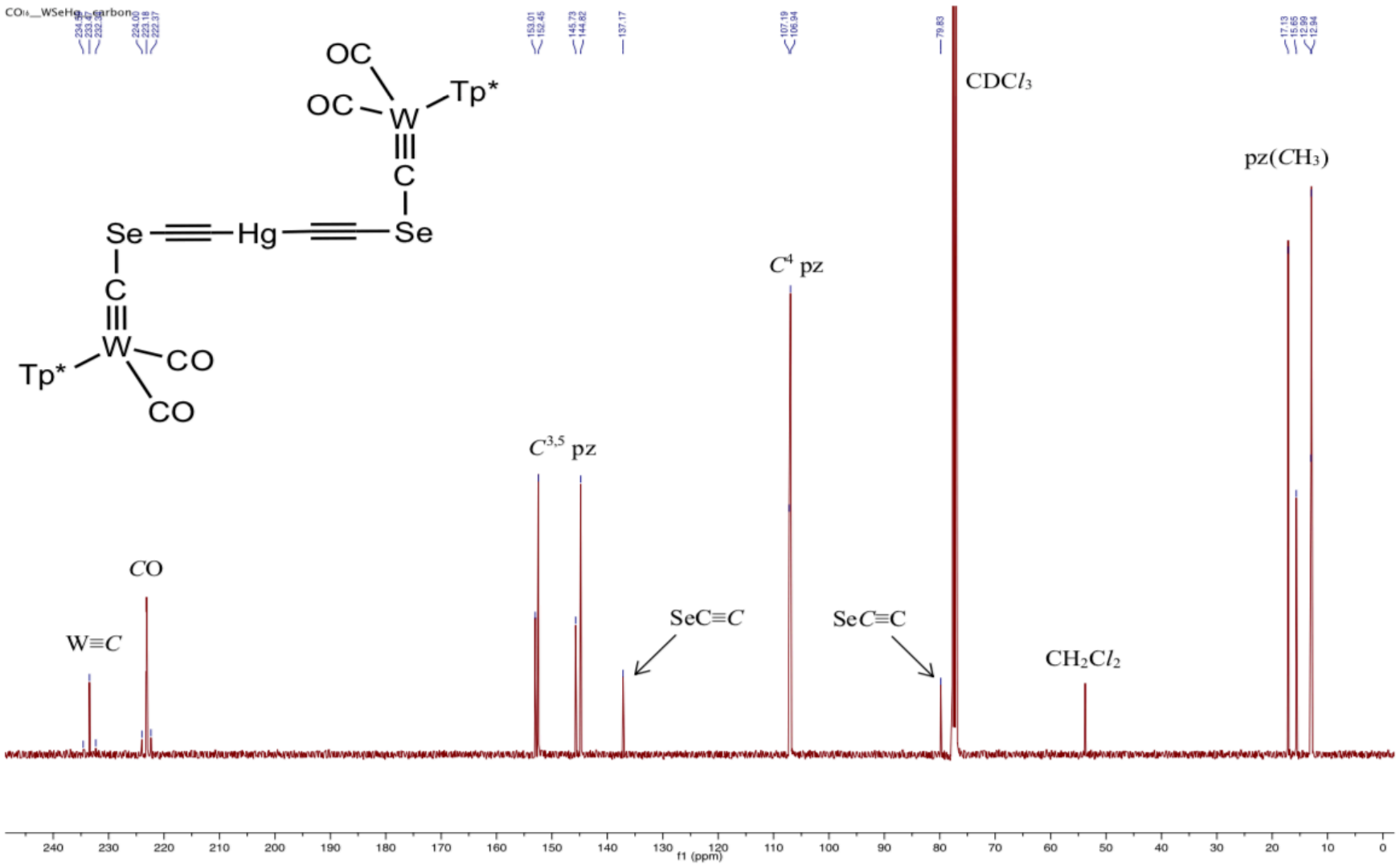


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$, 25 °C, δ) of Compound **3**.

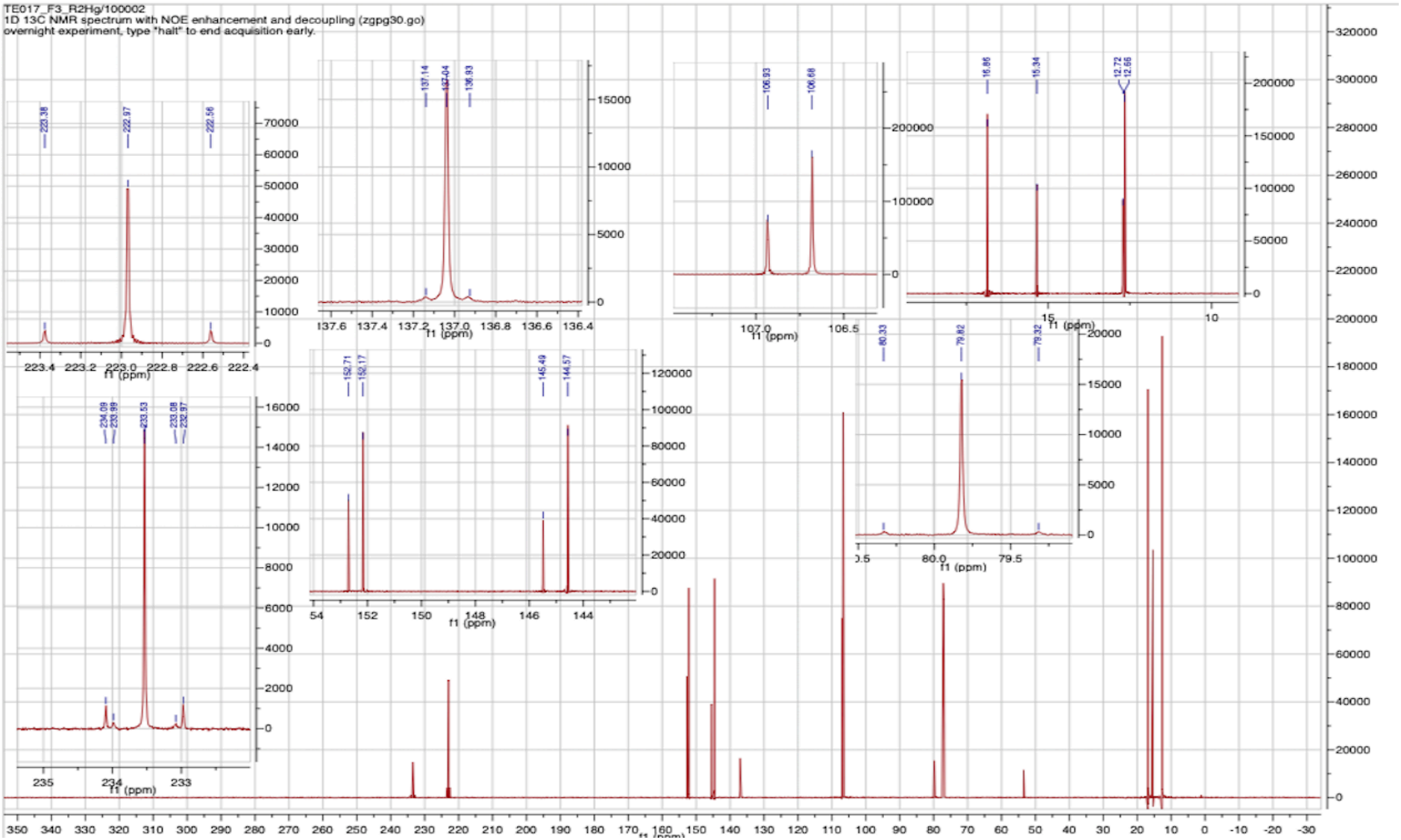


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (201 MHz, $CDCl_3$, 25 °C, δ) of Compound **3**.

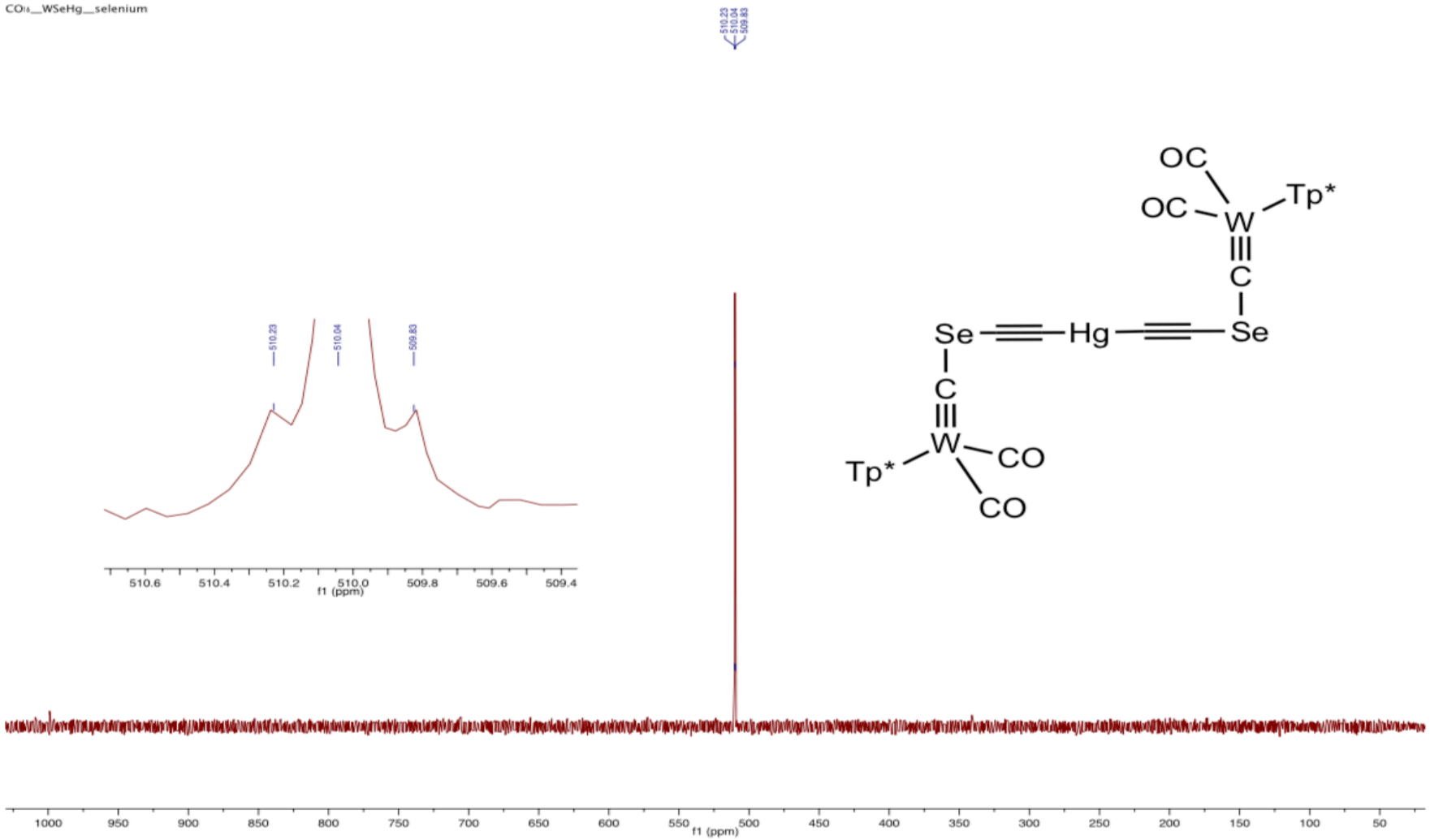


Figure S4. $^{77}Se\{^{1}H\}$ NMR spectrum (76 MHz, $CDCl_3$, 25 °C, δ) of Compound 3.

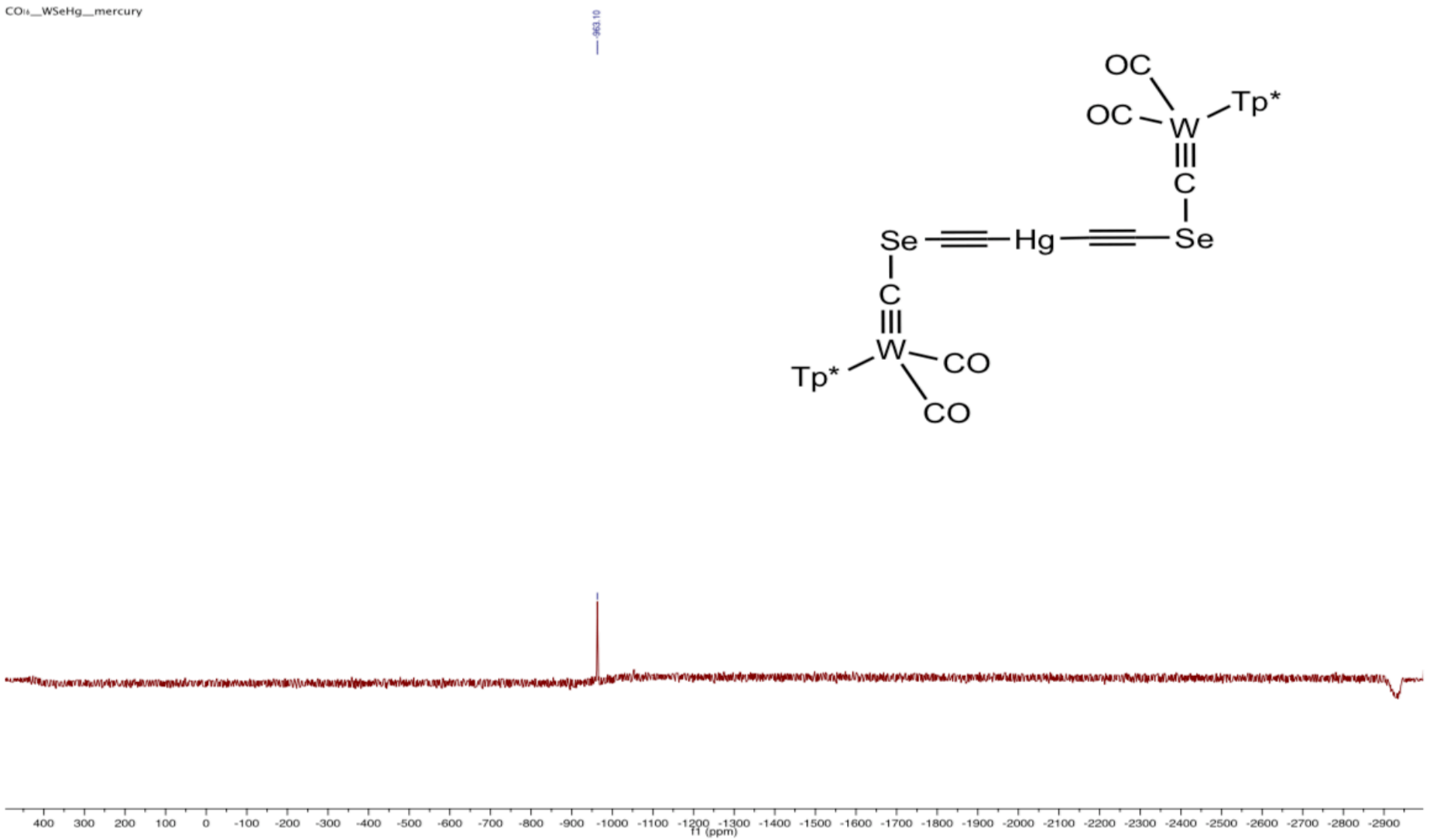


Figure S5. $^{199}Hg\{^{1}H\}$ NMR spectrum (72 MHz, $CDCl_3$, 25 °C, δ) of Compound **3**.

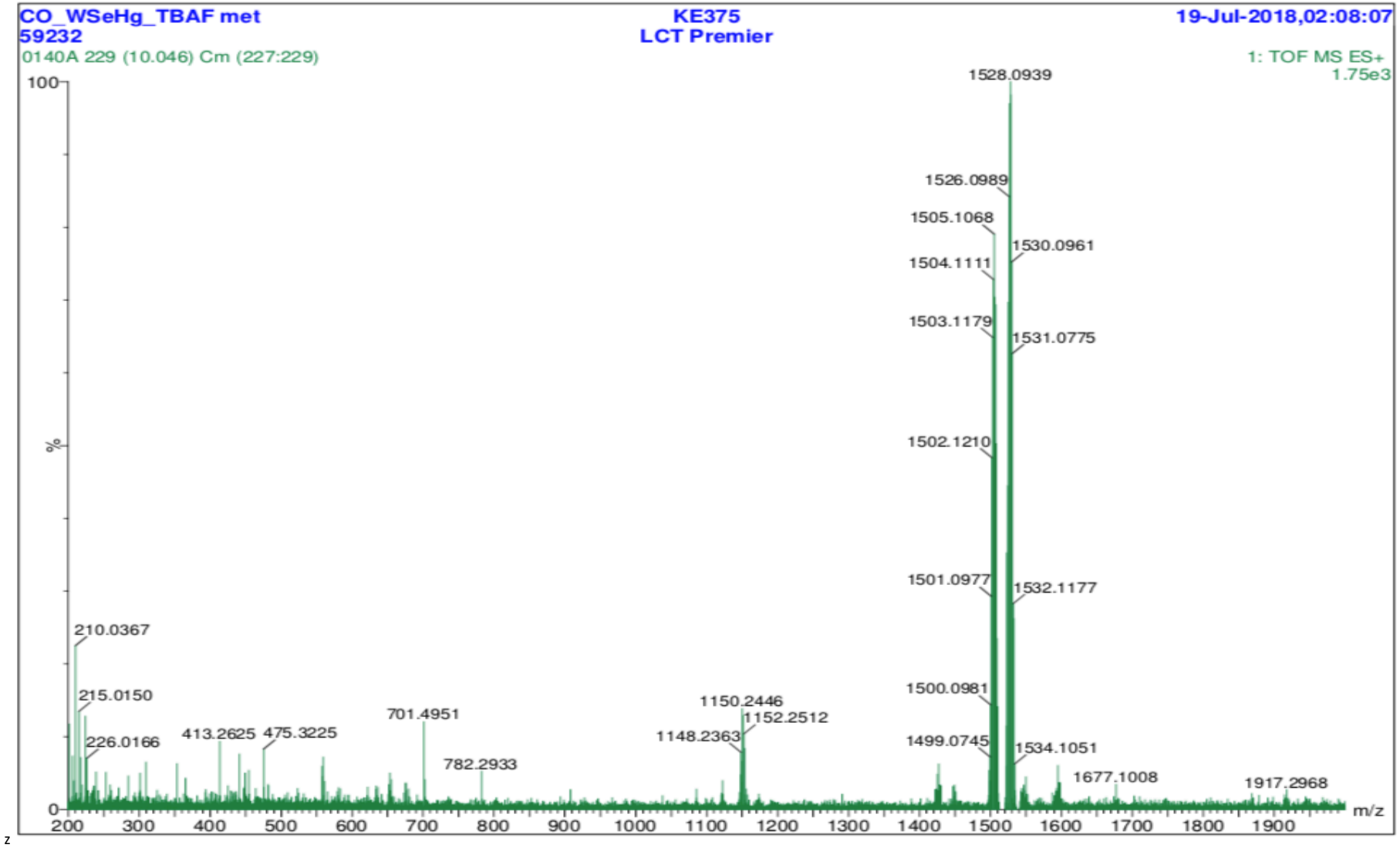


Figure S6. ESI-MS (+ve ion, MeCN matrix) of Compound **3**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -1.5, max = 35.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

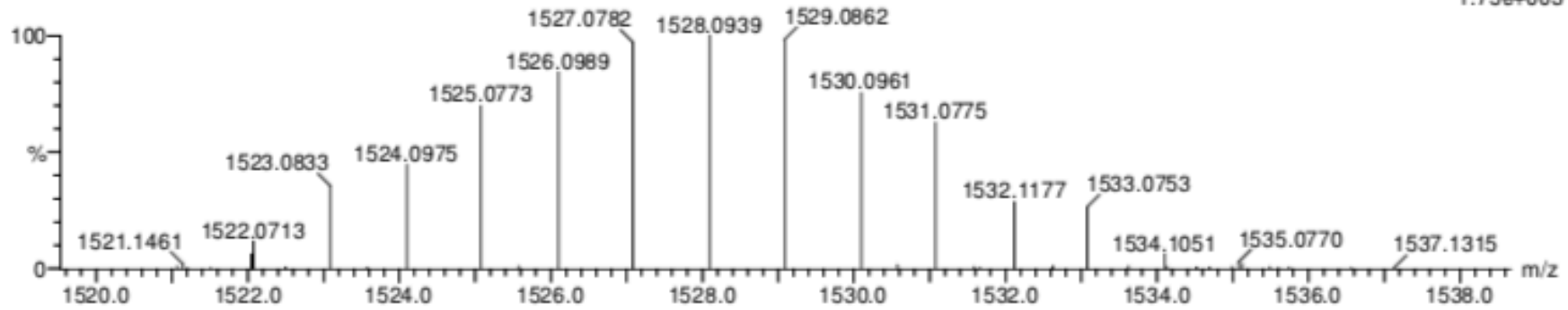
Monoisotopic Mass, Odd and Even Electron Ions
8976 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-40 H: 0-50 11B: 0-2 N: 0-13 O: 0-5 23Na: 0-1 80Se: 0-2 184W: 0-2 202Hg: 0-1

CO_WSeHg_TBAF met
59232
0140A 229 (10.046) Cm (227:229)

KE375
LCT Premier

19-Jul-2018,02:08:07

1: TOF MS ES+
1.75e+003



Minimum:				-1.5		
Maximum:		5.0	4.0	35.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
1531.0775	1531.0748	2.7	1.8	30.5	112.8	C40 H44 11B2 N12 O4 23Na 80Se2 184W2 202Hg

Figure S6 (cont.) . ESI-MS (+ve ion, MeCN matrix) of Compound **3**.

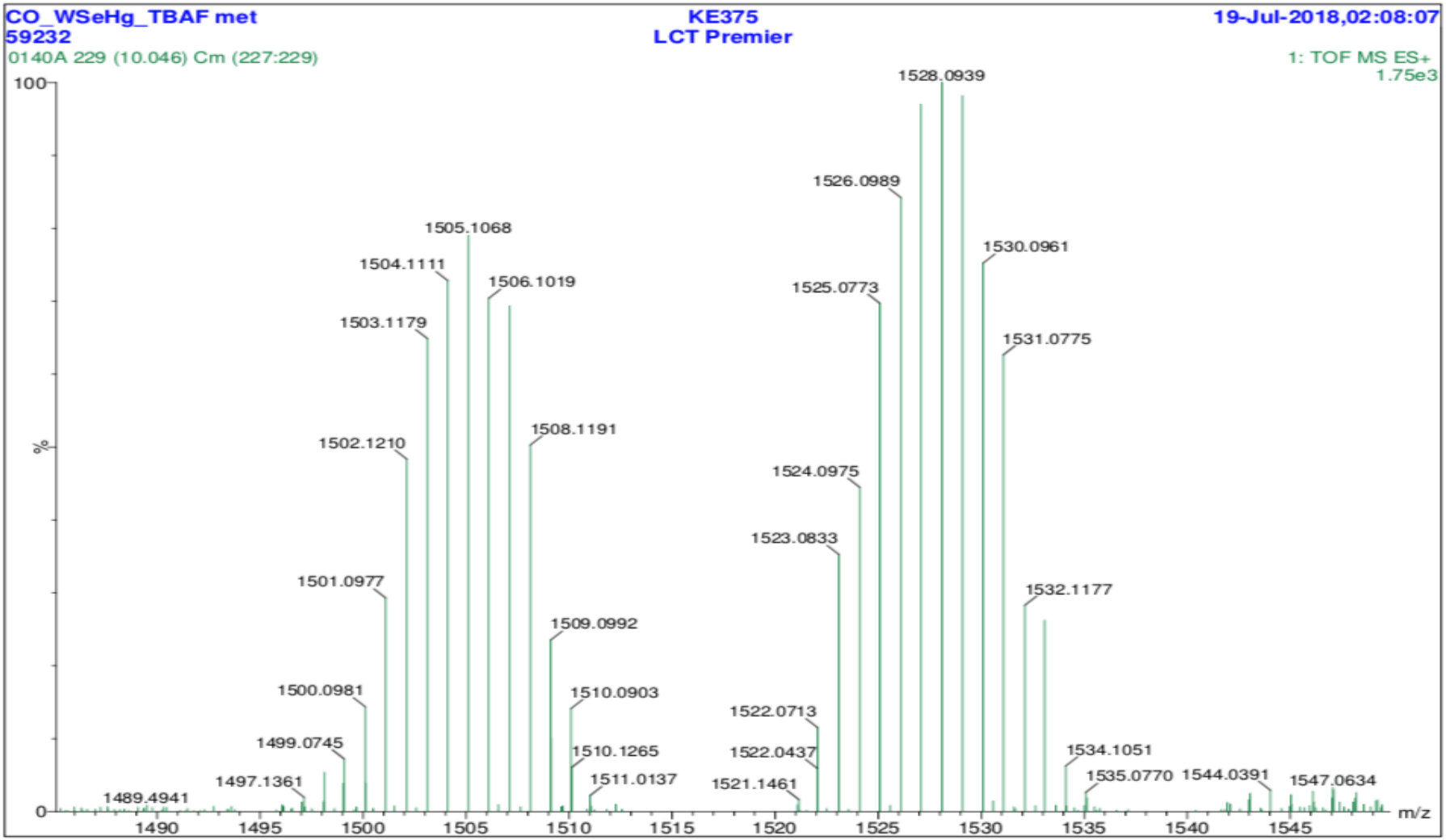


Figure S6 (cont.) . ESI-MS (+ve ion, MeCN matrix) of Compound **3**.

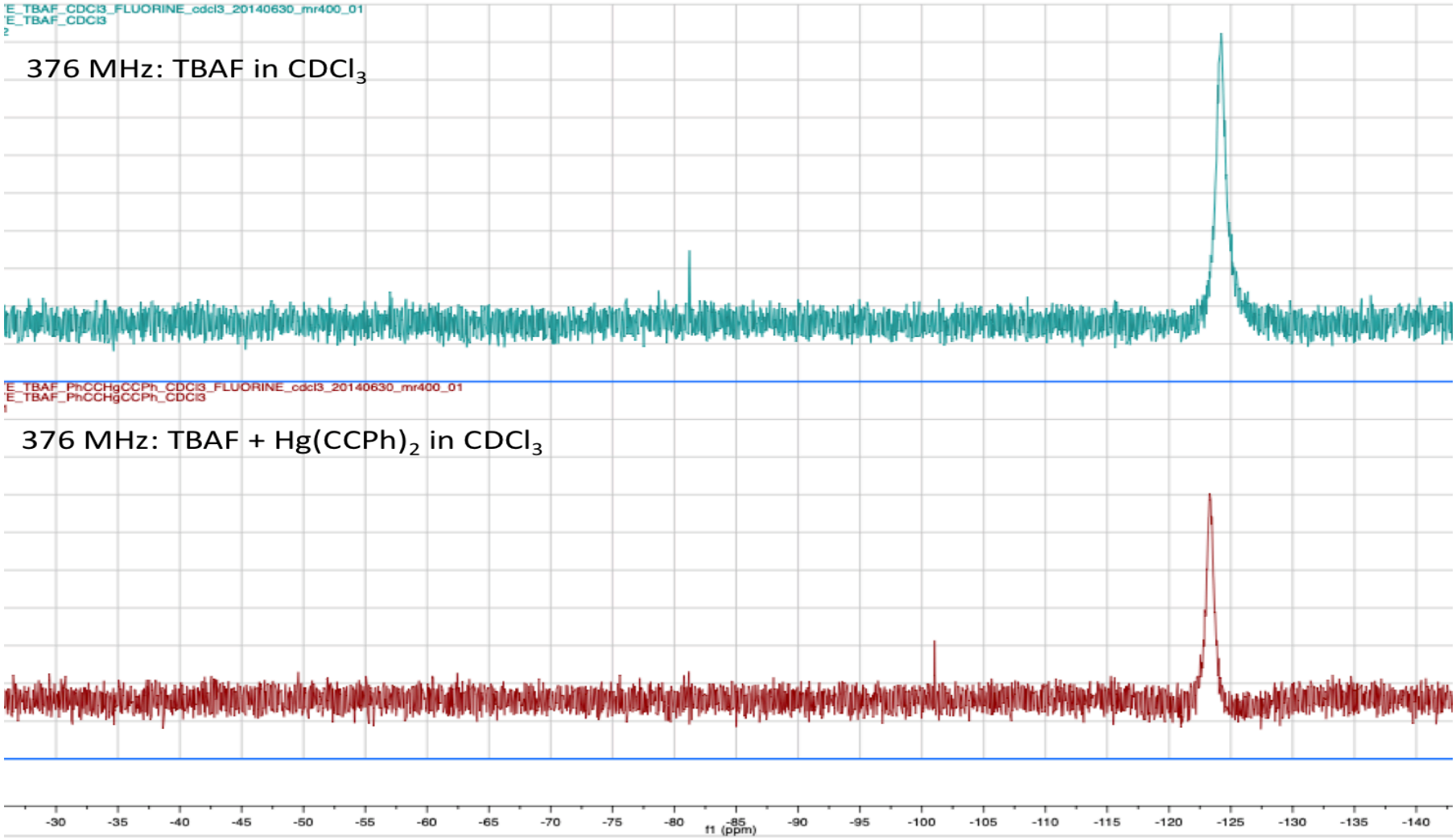


Figure S7 . $^{19}F\{^{1}H\}$ NMR spectrum of (a) $[^{n}Bu_4N]F$ and (b) $[^{n}Bu_4N]F$ + $Hg(CCPh)_2$ ($CDCl_3$, 376 MHz, 25 °C).

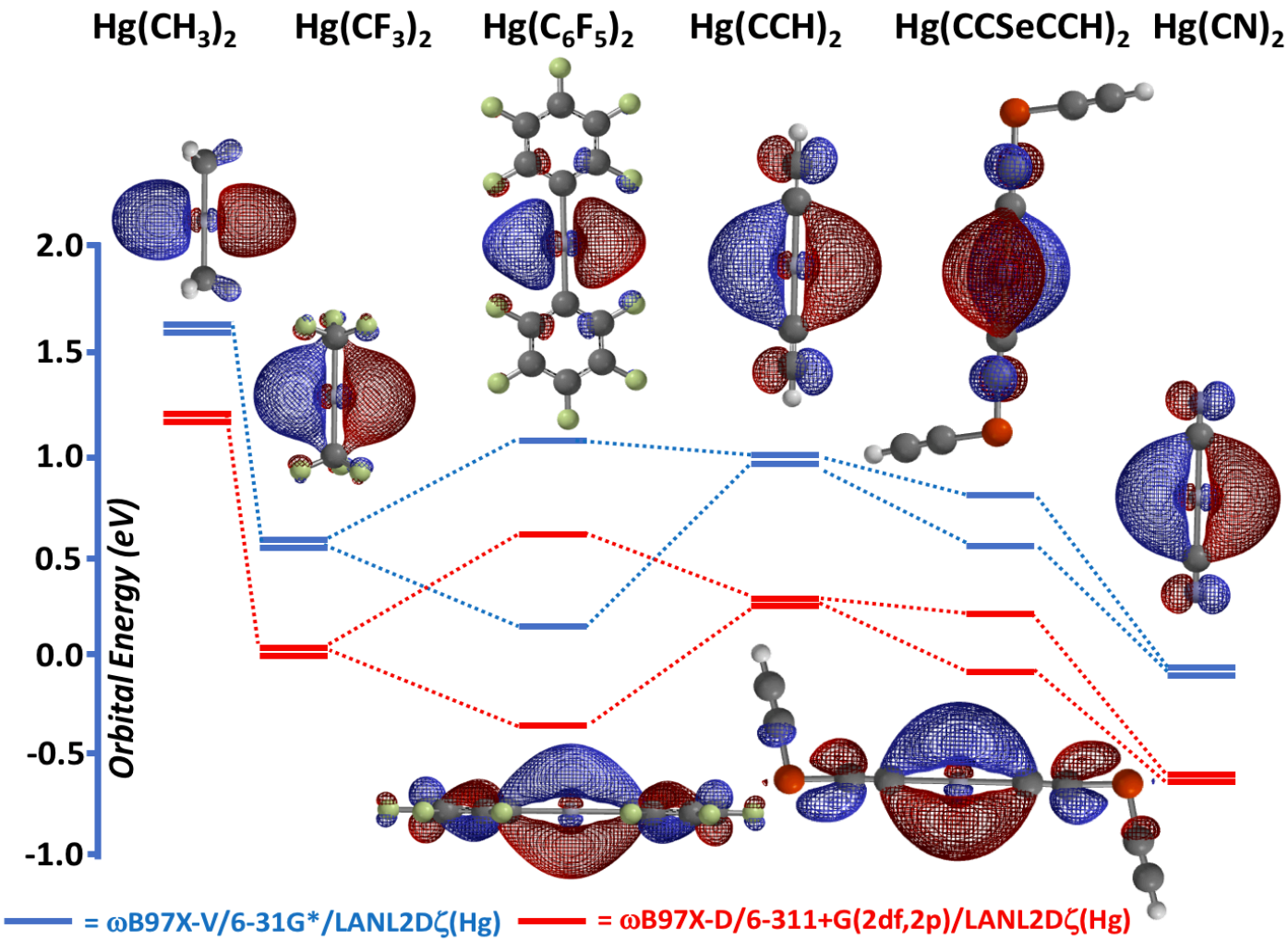


Figure S8. Basis set dependence of energies of mercury acceptor orbital. Blue = ωB97X-V/6-31G(d)/LANL2Dz(Hg); Red = ωB97X-D/6-311+G(2df,2p)/LANL2Dz(Hg). Orbitals depicted are for the larger basis set. See main paper for 6-31G(d) orbital depictions

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Optimised Geometries and Cartesian Coordinates

(a) [Hg(C≡CH)$_2$(phen)]

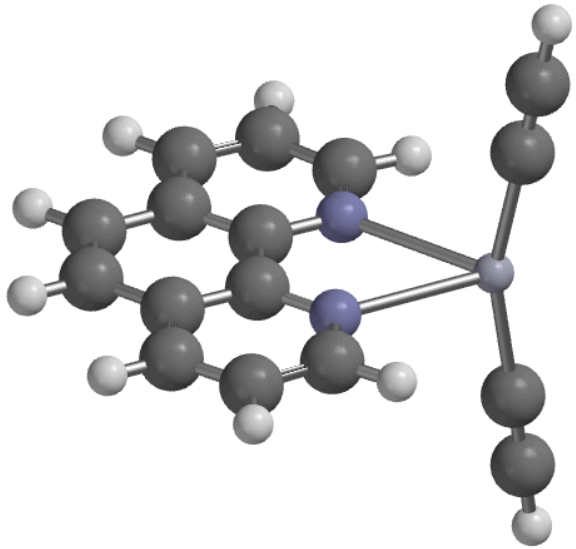

Figure S9: Optimised structure of [Hg(C≡CH)$_2$(phen)] (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg···N 2.684, 2.687 Å, Hg–C 2.151, 2.152 Å, C≡C 1.216 Å, C–Hg–C 160.9°.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9420): 2018, 2020 ν_{CC}.
Natural atomic charges of note: Hg (1.336), Cα (–0.584), N(–0.496).
Löwden bond orders of interest: Hg–C (0.93), Hg···N (0.27).

Table S1. Cartesian Coordinates for [Hg(C≡CH)$_2$(phen)]

Atom	x	y	z
Hg	0.021607	0.000999	-2.935796
C	0.024178	-2.121012	-3.291247
C	0.025836	-3.323440	-3.474040
H	0.027204	-4.377997	-3.645101
C	0.024577	2.122222	-3.294148
C	0.026678	3.324295	-3.479605
H	0.028426	4.378297	-3.653359
N	-1.374945	0.000925	-0.643937
C	-2.834518	-0.000775	1.728641
C	-0.731206	0.000105	0.542489
C	-2.694119	0.000998	-0.652889
C	-3.476081	0.000164	0.513600
C	-1.426086	-0.000808	1.771510
H	-3.167585	0.001715	-1.631335
H	-4.557944	0.000240	0.442288
H	-3.397288	-0.001471	2.658241
N	1.386663	0.001055	-0.621429
C	2.807371	-0.000459	1.774658
C	2.705690	0.001283	-0.608845
C	0.723694	0.000174	0.554339
C	1.398362	-0.000662	1.794530

Table S1 (cont.). Cartesian Coordinates for [Hg(C≡CH)$_2$(phen)]

Atom	x	y	z
C	3.468651	0.000553	0.570227
H	3.195077	0.002057	-1.579418
H	4.551522	0.000767	0.516449
H	3.354921	-0.001081	2.713285
C	-0.700426	-0.001725	3.010409
H	-1.263283	-0.002438	3.939556
C	0.652639	-0.001651	3.021419
H	1.200385	-0.002330	3.959510

Table S2: Thermodynamic Properties at 298.15 K

Zero Point Energy :	520.85	kJ/mol	(ZPE)
Temperature Correction :	42.75	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	563.60	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-767.306639	au	(Electronic Energy + Enthalpy Correction)
Entropy :	517.68	J/mol•K	
Gibbs Energy :	-767.365426	au	(Enthalpy - T*Entropy)
C_V :	285.80	J/mol•K	

(b) [Hg(C≡CSeMe)$_2$(phen)]

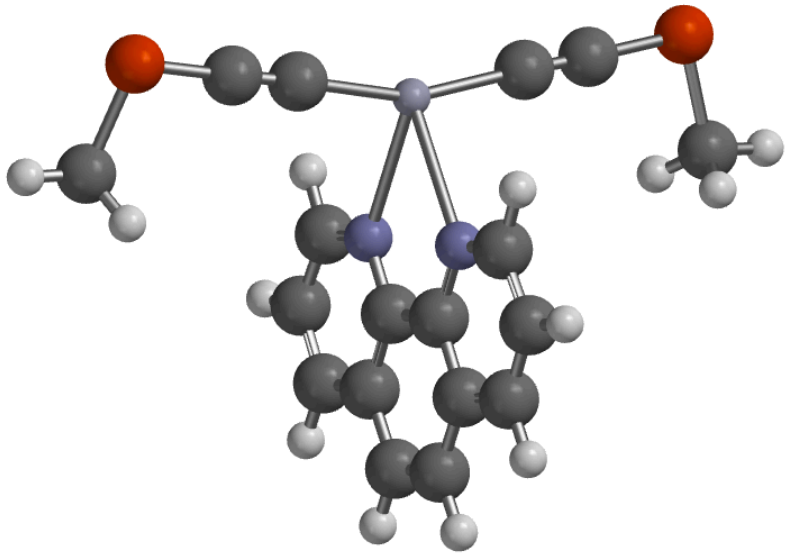

Figure S10: Optimised structure of [Hg(C≡CSeMe)$_2$(phen)] (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg···N 2.686, 2.690 Å, Hg–C 2.147, 2.148 Å, C≡C 1.222 Å, C–Hg–C 161.6°.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9420): 2090, 2092 ν_{CC}.
Natural atomic charges of note: Hg (1.343), Cα (–0.547), N(–0.497).
Löwden bond orders of interest: Hg–C (0.93), Hg···N (0.27).

Table S3. Cartesian Coordinates for [Hg(C≡CSeMe)$_2$(phen)]

Atom	x	y	z
Hg	-0.144237	0.000456	-2.582901
C	-0.133054	2.121825	-2.919354
C	-0.111994	3.334361	-3.069277
C	-0.145740	-2.118176	-2.933082
C	-0.135844	-3.330725	-3.083908
N	1.252285	-0.005703	-0.287975
C	2.713600	-0.008273	2.083453

Table S3 (cont.). Cartesian Coordinates for [Hg(C≡CSeMe)$_2$(phen)]

Atom	x	y	z
C	0.609521	-0.006127	0.899013
C	2.571523	-0.006249	-0.298277
C	3.354261	-0.007677	0.867786
C	1.305166	-0.007171	2.127568
H	3.043842	-0.005159	-1.277263
H	4.436068	-0.007837	0.795631
H	3.277223	-0.008939	3.012530
N	-1.508032	-0.001744	-0.264265
C	-2.928972	-0.004944	2.131697
C	-2.827263	-0.000798	-0.252221
C	-0.845348	-0.004708	0.911567
C	-1.519784	-0.005709	2.151819
C	-3.590075	-0.002550	0.927170
H	-3.316439	0.001434	-1.222889
H	-4.672937	-0.001736	0.873398
H	-3.476867	-0.005748	3.070139
C	0.579883	-0.005176	3.366758
H	1.142997	-0.005285	4.295729
C	-0.773273	-0.005448	3.378253
H	-1.320306	-0.005004	4.316802
Se	-0.139776	-5.145183	-3.352785
Se	-0.074511	5.148246	-3.337298
C	0.139905	5.681645	-1.461576
H	-0.711563	5.331004	-0.878223
H	0.180026	6.773305	-1.443670
H	1.068211	5.269118	-1.065986
C	0.579145	-5.659739	-1.602257
H	-0.093822	-5.321100	-0.814341
H	1.569737	-5.224458	-1.469300
H	0.646442	-6.750028	-1.592462

Table S4: Thermodynamic Properties at 298.15 K

Zero Point Energy :	666.26	kJ/mol	(ZPE)
Temperature Correction :	55.68	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	721.94	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-5648.503695	au	(Electronic Energy + Enthalpy Correction)
Entropy :	617.59	J/mol•K	
Gibbs Energy :	-5648.573828	au	(Enthalpy - T*Entropy)
C_V :	378.19	J/mol•K	

(c) [Hg(C≡CH)$_2$(py)$_2$]

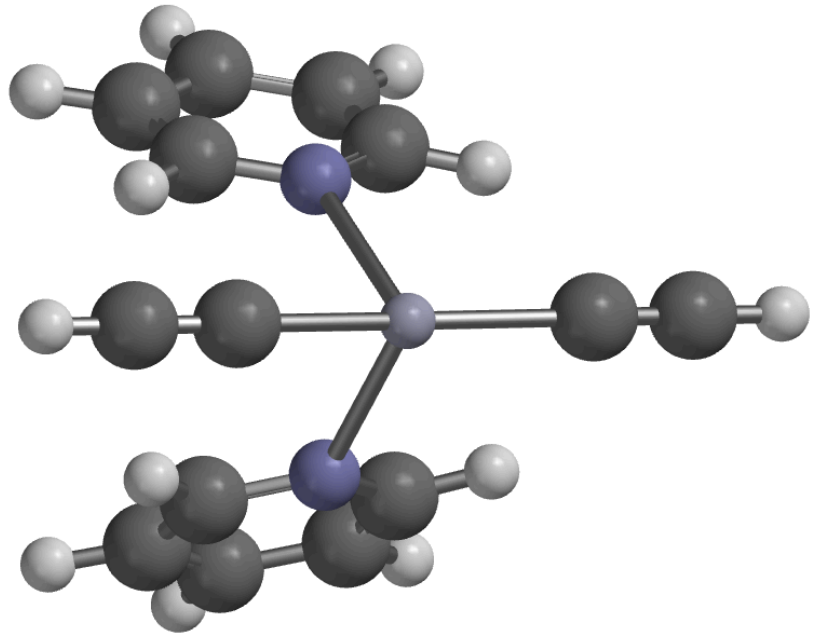

Figure S11: Optimised structure of [Hg(C≡CH)$_2$(py)2] (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg···N 2.637, 2.647 Å, Hg–C 2.164, 2.163 Å, C≡C 1.218, 1.217 Å, C–Hg–C 169.9°, N···Hg···N 74.51

Infrared absorptions of interest (cm^{-1}, scaled by 0.9420): 2008, 2014 ν_{CC}.
Natural atomic charges of note: Hg (1.357), Cα (–0.581), N(–0.549).

Löwden bond orders of interest: Hg–C (0.90), Hg···N (0.31).

Table S5. Cartesian Coordinates for [Hg(C≡CH)$_2$(py)2]

Atom	x	y	z
Hg	1.324886	-1.798568	1.464207
C	-0.410778	-2.457542	2.573172
C	-1.462529	-2.728803	3.122628
H	-2.364375	-2.995617	3.629752
C	3.247978	-1.401067	0.555896
C	4.256464	-1.070881	-0.041131
H	5.165456	-0.814777	-0.541295
N	0.593904	0.744984	1.472427
C	-0.524627	3.179243	0.742070
C	-0.654532	1.055351	1.832257
C	1.293797	1.628763	0.756403
C	0.775134	2.858027	0.365787
C	-1.253270	2.264738	1.498416
H	-1.184734	0.288682	2.392639
H	2.297903	1.313942	0.477518
H	1.375630	3.540071	-0.227574
H	-2.269518	2.475468	1.814432
H	-0.963671	4.129293	0.452142
N	-0.005325	-1.440922	-0.784521
C	-1.466218	-0.551131	-2.970391
C	0.610197	-0.897197	-1.837706
C	-1.337040	-1.538599	-0.796941
C	-2.109350	-1.107817	-1.869997
C	-0.079389	-0.440471	-2.954694
H	1.693791	-0.830588	-1.763244
H	-1.784825	-1.975964	0.094027
H	-3.189032	-1.208854	-1.839392
H	0.462253	-0.011635	-3.789891
H	-2.038181	-0.208132	-3.826997

Table S6: Thermodynamic Properties at 298.15 K

Zero Point Energy :	541.31	kJ/mol	(ZPE)
Temperature Correction :	42.53	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	583.84	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-692.295427	au	(Electronic Energy + Enthalpy Correction)
Entropy :	518.42	J/mol•K	
Gibbs Energy :	-692.354299	au	(Enthalpy - T*Entropy)
C_V :	282.37	J/mol•K	

(d)[Hg(C≡CH)$_2$(F)]$^-$

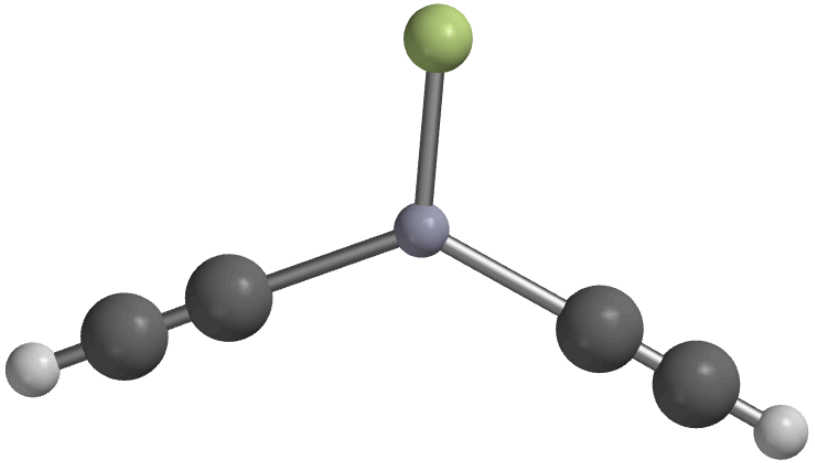

Figure S12: Optimised structure of [Hg(C≡CH)$_2$(F)]$^-$ (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg···F 2.133 Å, Hg–C 2.238, 2.139, 2.163 Å, C≡C 1.218, 1.217 Å, C–Hg–C 169.9°, N···Hg···N 74.51

Infrared absorptions of interest (cm^{-1}, scaled by 0.9420): 2008, 2014 ν_{CC}.
Natural atomic charges of note: Hg (1.358), Cα (–0.563), F(–0.793).
Löwden bond orders of interest: Hg–C (0.87), Hg···F (0.88).

Table S7. Cartesian Coordinates for $[Hg(C{\equiv}CH)_2(F)]^-$

Atom	x	y	z
Hg	0.000288	0.000000	-0.807871
C	-2.033964	0.000000	0.125886
C	-3.137321	0.000000	0.648097
H	-4.105104	0.000000	1.100439
C	2.035745	0.000000	0.123809
C	3.137594	0.000000	0.648759
H	4.104566	0.000000	1.102022
F	-0.001805	0.000000	-2.941140

Table S8: Thermodynamic Properties at 298.15 K

Zero Point Energy :	89.51	kJ/mol	(ZPE)
Temperature Correction :	23.23	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	112.73	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-295.905404	au	(Electronic Energy + Enthalpy Correction)
Entropy :	379.95	J/mol•K	
Gibbs Energy :	-295.948552	au	(Enthalpy - T*Entropy)
C_V :	117.78	J/mol•K	

(d)$[Hg(C{\equiv}CH)_2(dmso)_4]$

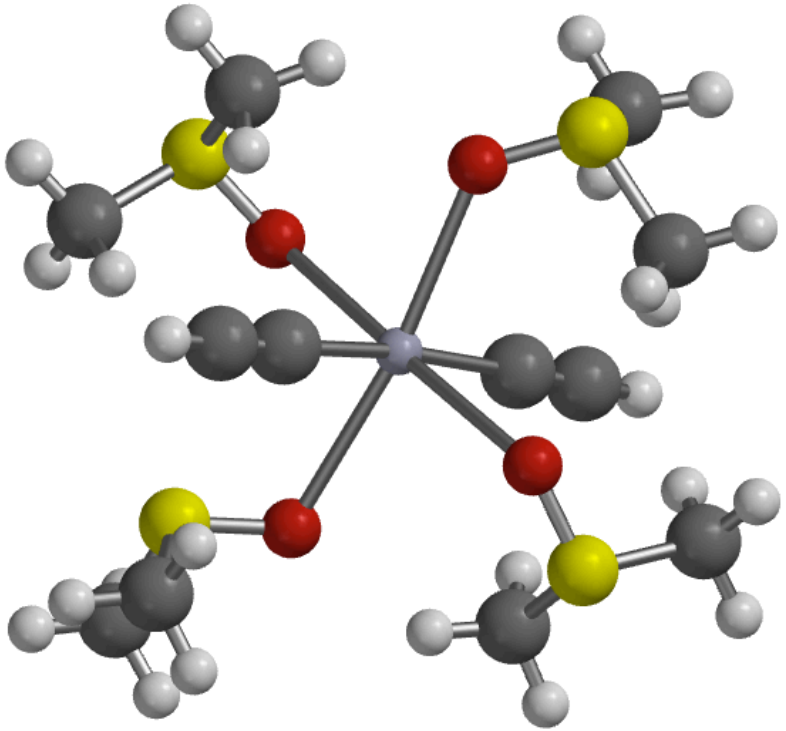

Figure S13: Optimised structure of $[Hg(C{\equiv}CH)_2(dmso)_4]$ (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg···O 2.621, 2.724, 2.754, 2.684 Å, Hg–C 2.2190, 2,217 Å, C≡C 1.222, 1.222 Å, C–Hg–C 174.3°.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9420): 2008, 2014 ν_{CC}.
Natural atomic charges of note: Hg (1.358), Cα (–0.563), F(–0.793).
Löwden bond orders of interest: Hg–C (0.87), Hg···F (0.88).

Table S9. Cartesian Coordinates for $[Hg(C{\equiv}CH)_2(dmso)_4]$

Atom	x	y	z
Hg	0.307066	0.017572	-0.137230

Table S9 (cont). Cartesian Coordinates for $[Hg(C{\equiv}CH)_2(dmso)4]$

C	-0.794287	0.295439	-2.043119
C	-1.387174	0.448831	-3.100044
H	-1.885508	0.613269	-4.031317
C	1.254507	-0.132184	1.860994
C	1.762122	-0.206501	2.969706
H	2.200730	-0.313408	3.938580
O	-0.355803	2.598882	0.558089
O	1.002440	-2.425882	-0.782536
O	2.599637	0.737261	-1.333510
O	-2.077741	-0.961262	0.797761
S	-1.032043	3.035155	1.839985
S	-2.874488	-1.702039	-0.254678
S	3.710253	1.562321	-0.713805
S	1.274016	-3.001182	-2.158315
C	-1.764935	1.574540	2.619552
H	-2.443665	1.116386	1.897569
H	-2.308450	1.893683	3.514252
H	-0.987155	0.846047	2.862996
C	0.277647	3.281433	3.070436
H	0.876987	2.367902	3.128154
H	-0.174509	3.516033	4.038549
H	0.891410	4.121134	2.736376
C	-4.032950	-2.738301	0.677278
H	-4.738052	-3.219995	-0.006156
H	-4.560526	-2.120690	1.409212
C	-4.086650	-0.524818	-0.898624
H	-4.620891	-0.060024	-0.064891
H	-4.781080	-1.037172	-1.570724
H	-3.510574	0.221341	-1.450463
C	-0.337934	-3.213177	-2.958900
H	-0.878107	-3.983420	-2.404262
H	-0.188780	-3.534840	-3.993949
H	-0.878564	-2.263055	-2.913679
C	4.564680	0.481205	0.460795
H	5.073974	-0.292908	-0.117135

Table S9 (cont). Cartesian Coordinates for $[Hg(C{\equiv}CH)_2(dmso)_4]$

H	3.823850	0.029317	1.127322
H	5.298454	1.066232	1.023213
C	2.955938	2.664618	0.509366
H	3.725767	3.340259	0.894506
H	2.506006	2.071898	1.309059
H	2.169680	3.224461	-0.001336
H	-3.442613	-3.495608	1.197182
C	1.872327	-1.670373	-3.229297
H	2.749900	-1.234910	-2.748944
H	1.111504	-0.891902	-3.327458
H	2.133585	-2.101571	-4.200559

Table S10: Thermodynamic Properties at 298.15 K

Zero Point Energy :	903.96	kJ/mol	(ZPE)
Temperature Correction :	77.46	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	981.42	kJ/mol	(ZPE + temperature correction)
Enthalpy :	-2408.272604	au	(Electronic Energy + Enthalpy Correction)
Entropy :	744.21	J/mol•K	
Gibbs Energy :	-2408.357116	au	(Enthalpy - T*Entropy)
C_V :	509.78	J/mol•K	

$[Hg(C{\equiv}CH)_2]$

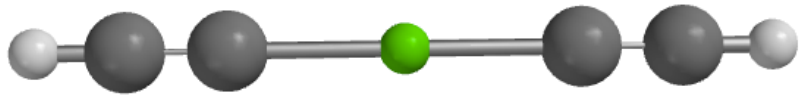

Figure S14: Optimised structure of $[Hg(C{\equiv}CH)_2]$ (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg–C 2.102, 2.103Å, C≡C 1.215, 1.214 Å, C–Hg–C 180.0°.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9420): 2166, 2170 ν_{CC}.
Natural atomic charges of note: Hg (1.280), Cα (–0.614).
Löwden bond orders of interest: Hg–C (0.97).

Table S11. Cartesian Coordinates for $[Hg(C{\equiv}CH)_2]$

Atom	x	y	z
Hg	0.000187	0.000000	0.000510
C	-2.102856	0.000000	-0.002359
C	2.101872	0.000000	0.002007
H	4.386933	0.000000	-0.001161
C	3.316266	0.000000	0.000679
H	-4.388377	0.000000	-0.012221
C	-3.317653	0.000000	-0.007397

Table S12: Thermodynamic Properties at 298.15 K

Zero Point Energy :	96.09	kJ/mol	(ZPE)
Temperature Correction :	18.69	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	114.78	kJ/mol	(ZPE + temperature correction)
Enthalpy :	–196.032858	au	(Electronic Energy + Enthalpy Correction)
Entropy :	294.57	J/mol•K	
Gibbs Energy :	-–196.066308	au	(Enthalpy - T*Entropy)
C_V :	88.09	J/mol•K	

$[Hg(C{\equiv}N)_2]$

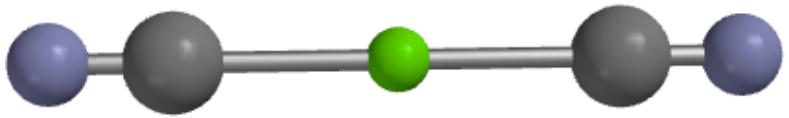

Figure S15: Optimised structure of $[Hg(C{\equiv}N)_2]$ (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg–C 2.115, Å, C≡N 1.162, 1.1652 Å, C–Hg–C 180.0°.

Infrared absorptions of interest (cm^{-1}, scaled by 0.9420): 2351, 2353 ν_{CN}.
Natural atomic charges of note: Hg (1.294), Cα (–0.311).
Löwden bond orders of interest: Hg–C (0.93).

Table S13. Cartesian Coordinates for $[Hg(C{\equiv}N)_2]$

Atom	x	y	z
Hg	0.000000	0.000000	0.000000
C	0.000000	0.000000	-2.114721
N	0.000000	0.000000	-3.276756
C	0.000000	0.000000	2.114721
N	0.000000	0.000000	3.276756

Table S14: Thermodynamic Properties at 298.15 K

Zero Point Energy :	39.65	kJ/mol	(ZPE)
Temperature Correction :	17.61	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	57.26	kJ/mol	(ZPE + temperature correction)
Enthalpy :	–228.254776	au	(Electronic Energy + Enthalpy Correction)
Entropy :	305.19	J/mol•K	
Gibbs Energy :	-–2278.289433	au	(Enthalpy - T*Entropy)
C_V :	79.11	J/mol•K	

[Hg(C$_6$F$_5$)$_2$]

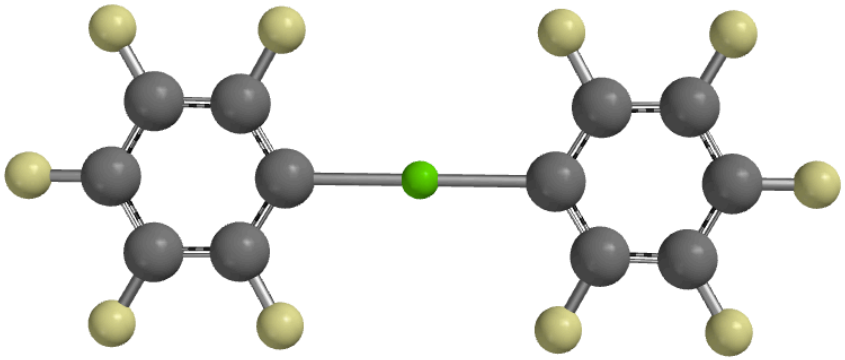

Figure S16: Optimised structure of [Hg(C$_6$F$_5$)$_2$] (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg–C 2.164, Å, C–Hg–C 180.0°.

Natural atomic charges of note: Hg (1.252), Cα (–0.635).
Löwden bond orders of interest: Hg–C (0.84).

Table S1. Cartesian Coordinates for [Hg(C$_6$F$_5$)$_2$]

Atom	x	y	z
Hg	-0.000000	0.000000	0.000000
C	-0.000000	0.000000	-2.164153
C	0.000000	0.000000	-4.968928
C	1.182404	0.000000	-2.885928
C	-1.182404	0.000000	-2.885928
C	-1.207708	0.000000	-4.276177
C	1.207708	0.000000	-4.276177
C	-0.000000	0.000000	2.164153
C	0.000000	0.000000	4.968928
C	-1.182404	0.000000	2.885928
C	1.182404	0.000000	2.885928
C	1.207708	0.000000	4.276177
C	-1.207708	0.000000	4.276178
F	2.361338	0.000000	-2.231271
F	2.361696	0.000000	-4.949941
F	0.000000	0.000000	-6.302248
F	-2.361696	0.000000	-4.949942
F	-2.361338	0.000000	-2.231271
F	2.361338	0.000000	2.231271
F	2.361696	0.000000	4.949941
F	0.000000	0.000000	6.302248
F	-2.361338	0.000000	2.231271
F	-2.361696	0.000000	4.949942

Table S2: Thermodynamic Properties at 298.15 K

Zero Point Energy :	261.12	kJ/mol	(ZPE)
Temperature Correction :	48.09	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	309.21	kJ/mol	(ZPE + temperature correction)
Enthalpy :	–1497.673908	au	(Electronic Energy + Enthalpy Correction)
Entropy :	548.13	J/mol•K	
Gibbs Energy :	–1497.736153	au	(Enthalpy - T*Entropy)
C_V :	304.88	J/mol•K	

$[Hg(CF_3)_2]$

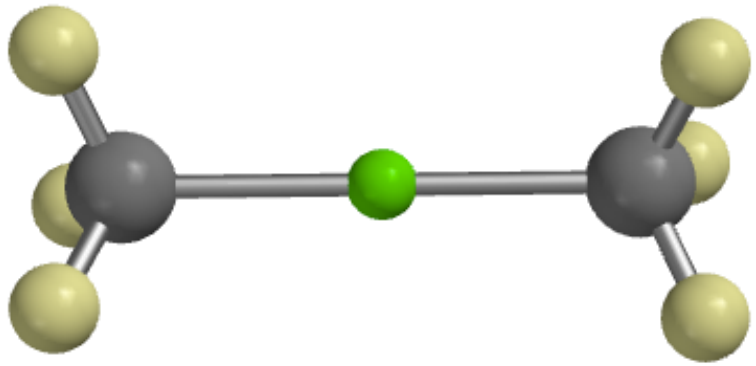

Figure S17: Optimised structure of $[Hg(CF_3)_2]$ (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg–C 2.228, Å, C–Hg–C 180.0°.

Natural atomic charges of note: Hg (1.064), Cα (+0.614).
Löwden bond orders of interest: Hg–C (0.81).

Table S1. Cartesian Coordinates for $[Hg(CF_3)_2]$

Atom	x	y	z
Hg	-0.000837	0.000727	-0.000266
C	-0.000217	0.000065	2.228456
C	-0.000133	0.000237	-2.228739
F	1.251812	-0.081128	2.738803
F	-0.555542	1.124229	2.740663
F	-0.695695	-1.043641	2.739755
F	1.190646	-0.395305	-2.738564
F	-0.252804	1.228390	-2.740551
F	-0.937230	-0.833574	-2.739557

Table S2: Thermodynamic Properties at 298.15 K

Zero Point Energy :	70.01	kJ/mol	(ZPE)
Temperature Correction :	24.22	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	94.23	kJ/mol	(ZPE + temperature correction)
Enthalpy :	–717.634589	au	(Electronic Energy + Enthalpy Correction)
Entropy :	397.65	J/mol•K	
Gibbs Energy :	-–717.679746	au	(Enthalpy - T*Entropy)
C_V :	129.29	J/mol•K	

$[Hg(CH_3)_2]$

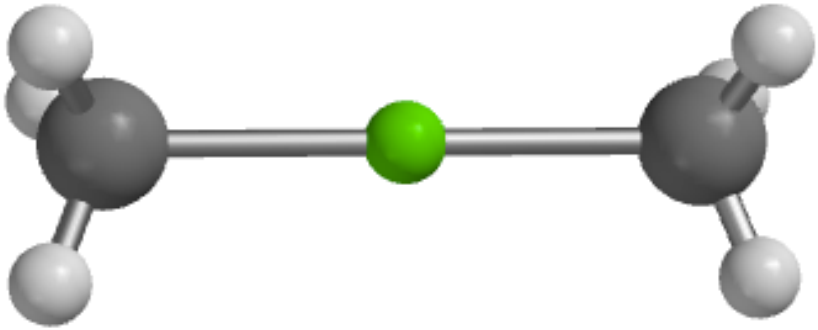

Figure S18: Optimised structure of $[Hg(CH_3)_2]$ (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg–C 2.197 Å, C–Hg–C 180.0°.

Natural atomic charges of note: Hg (1.099), Cα (–1.247).
Löwden bond orders of interest: Hg–C (0.98).

Table S1. Cartesian Coordinates for $[Hg(CH_3)_2]$

Atom	x	y	z
Hg	0.000374	0.000000	0.000000
C	0.000054	0.000000	-2.197038
H	1.024925	-0.000000	-2.586229

H	-0.512583	0.887667	-2.585763
H	-0.512583	-0.887667	-2.585763
C	0.000054	0.000000	2.197038
H	1.024925	-0.000001	2.586229
H	-0.512583	-0.887666	2.585763
H	-0.512582	0.887667	2.585763

Table S2: Thermodynamic Properties at 298.15 K

Zero Point Energy :	187.99	kJ/mol	(ZPE)
Temperature Correction :	16.19	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	204.18	kJ/mol	(ZPE + temperature correction)
Enthalpy :	–122.351242	au	(Electronic Energy + Enthalpy Correction)
Entropy :	305.69	J/mol•K	
Gibbs Energy :	–122.385956	au	(Enthalpy - T*Entropy)
C_V :	76.68	J/mol•K	

[$HgCl_2$]

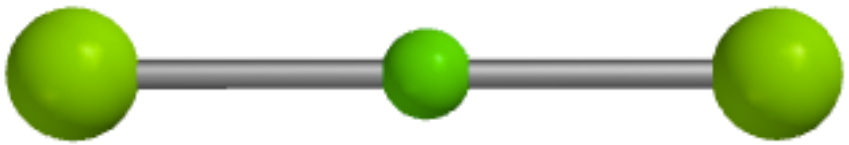

Figure S19: Optimised structure of [$HgCl_2$] (ωB97X-V/6-31G*/LANL2Dζ/gas phase). Bond lengths (Å) and angles (°) of interest: Hg–Cl 2.362 Å, Cl–Hg–Cl 180.0°.

Natural atomic charges of note: Hg (1.323), Cα (–0.661).
Löwden bond orders of interest: Hg–Cl (1.23).

Table S1. Cartesian Coordinates for [$HgCl_2$]

Atom	x	y	z
Hg	0.000000	0.000000	0.000000
Cl	0.000000	0.000000	-2.361648
Cl	0.000000	0.000000	2.361648

Table S2: Thermodynamic Properties at 298.15 K

Zero Point Energy :	5.10	kJ/mol	(ZPE)
Temperature Correction :	13.07	kJ/mol	(vibration + gas law + rotation + translation)
Enthalpy Correction :	18.18	kJ/mol	(ZPE + temperature correction)
Enthalpy :	–962.966569	au	(Electronic Energy + Enthalpy Correction)
Entropy :	278.32	J/mol•K	
Gibbs Energy :	–962.998175	au	(Enthalpy - T*Entropy)
C_V :	50.43	J/mol•K	

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