Supplementary information for the manuscript

"Volatile heterometallics: structural diversity of palladium-lead β-diketonates and correlation with thermal properties" by V.V. Krisyuk, I.A. Baidina, N.A. Kryuchkova, V.A. Logvinenko, P.E. Plyusnin, I.V. Korolkov, G.I. Zharkova, A.E. Turgambaeva, I.K. Igumenov

Content

Table S1. Crystallographic Data and XRD Experiment Details.

Compound	*[3Pd(acac)$_2$*2[Pb(hfac)$_2$] (**1**)*	*[Pd(hfac)$_2$*2[Pb(hfac)$_2$] (**2**)*
Stoichiometric formula	C12.50 H11.50 F6 O5 Pb0.50 Pd0.75	C20 H4 F24 O8 PbPd
Molecular weight	539.11	1141.82
Temperature	150(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	triclinic	triclinic
Space group	P-1	*P*-1
Unit cell parameters	a= 9.8703(6) Å α= 74.659(2)° b= 13.2237(9) Å β= 72.712(2)° c= 14.5931(9) Å γ= 69.401(2)°	*a*= 9.4437(16) Å α = 91.519(5)° *b*= 11.538(2) Å β = 91.672(5)° *c*= 14.995(3) Å γ = 97.940(5)°
Volume	1674.89(18) Å^3	1616.7(5) Å^3
Z	4	2
Density (calculated)	2.138 g/cm^3	2.346 g/cm^3
Absorption coefficient	5.933 mm^{-1}	5.937 mm^{-1}
F(000)	1024	1064
Crystal size	0.40 x 0.15 x 0.11 mm^3	0.17 x 0.07 x 0.03 mm^3
θ record area	2.03 - 31.56°	2.18 - 30.62°.
h, k, l range	-14<=h<=14, -19<=k<=19, -21<=l<=18	-13<=h<=12, -16<=k<=16, -21<=l<=21
Number of measured/independent reflections	20943/10837 [R(int) = 0.0436]	29916/9628 [R(int)= 0.0814]
Completeness of data collection on θ = 25.00°	98.3 %	97.7 %
Max and min transmission	0.5614 and 0.2000	0.8420 and 0.4318
Refinement method	full matrix LSM against F^2	full matrix LSM against F^2
Number of reflections/limits/parameters	10837 / 0 / 481	9628 / 0 / 484
S factor against F^2	0.993	0.871
R factor [I > 2σ(I)]	R1 = 0.0412, wR2 = 0.0722	R1 = 0.0575, wR2 = 0.1241
R factor (all data)	R1 = 0.0610, wR2 = 0.0770	R1 = 0.1667, wR2 = 0.1508
Max and min residual electron density	1.730 and -1.108 e/Å^3	1.454 and -1.074 e/Å^3

Quantum chemistry computations

Quantum chemistry calculations of the electronic structure of pentanuclear complex ***1*** were carried out Jaguar 7.5 program, Schrödinger Inc. [1]. For geometry optimization the method of DFT with hybrid exchange and correlation functional of B3LYP [2,3] was chosen. Basis sets *lacvp* and *lacv3p* [4] that include effective core potentials for atoms Pd and Pb respectively were used. Basis sets *6-31G* [5] – for other atoms which constitute the complex ***1***. Computed structural data agree well with those ones from XRD. The deviation of average distances Pd-O and Pb-O from experimental ones does not exceed 0.05 – 0.015 Å. Effective charges on atoms were defined from the molecular electrostatic potential (ESP) [6,7]. The investigation of molecular orbitals was performed by NBO analysis [8]. Summary of NBO analysis for ***1*** is presented in the **Annex I**.

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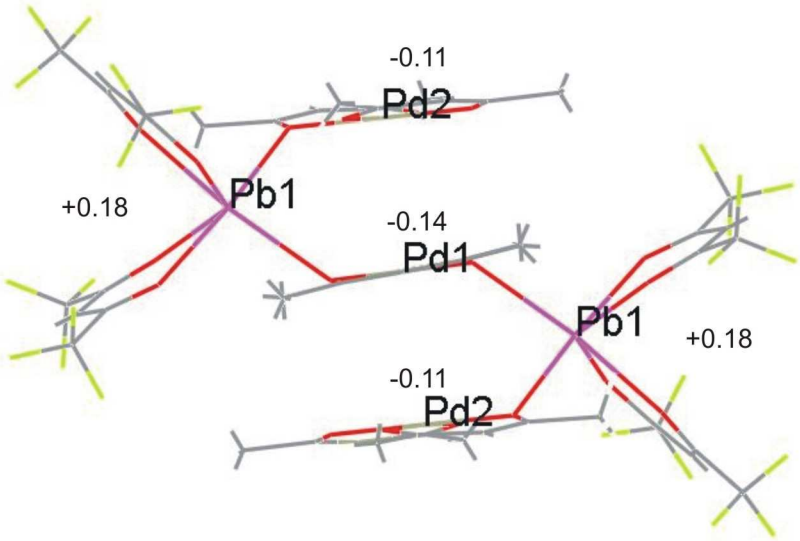

Fig. S1. Charge distribution on molecules of metal β-diketonates forming a heterocomplex ***1***

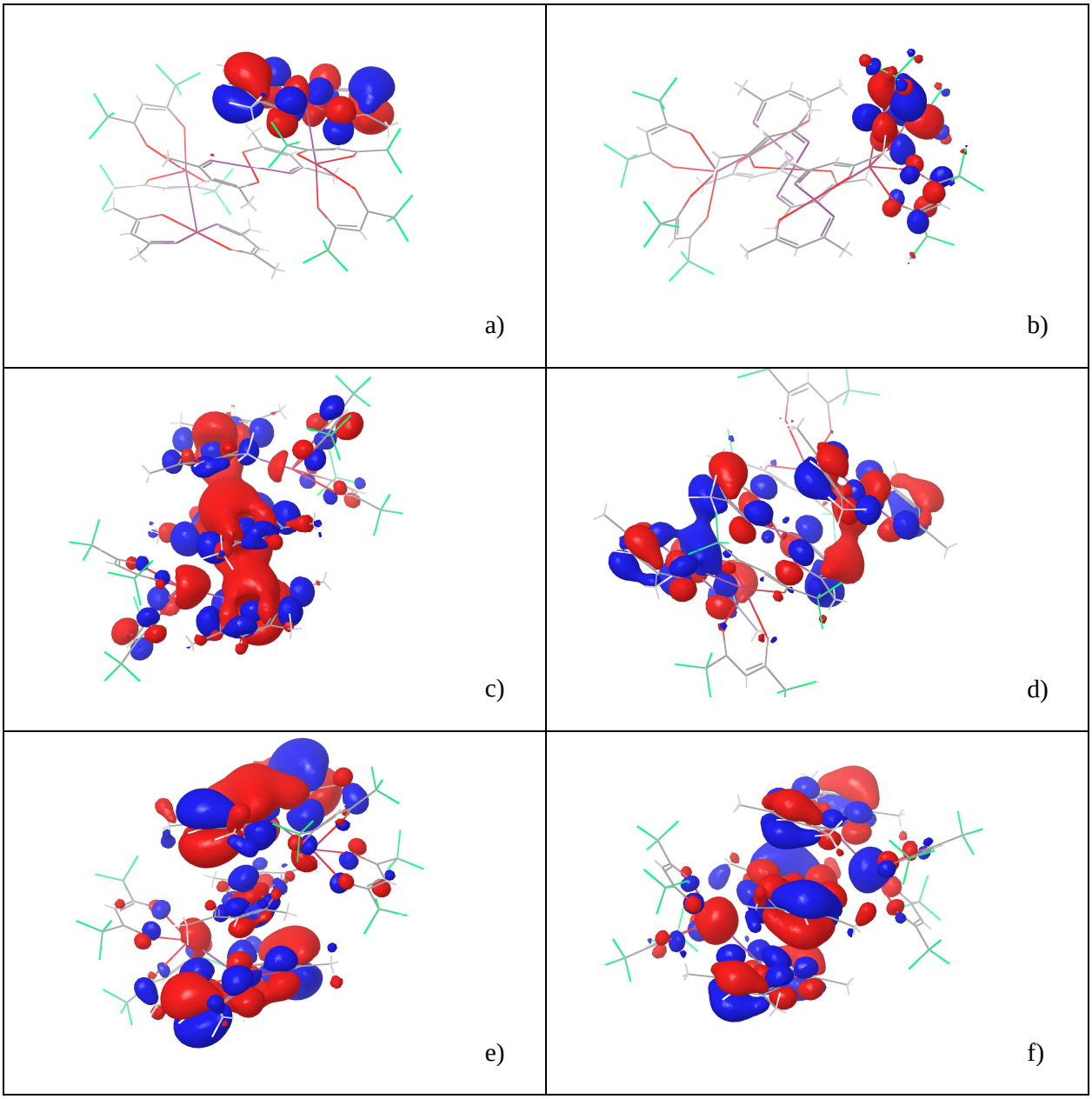

Fig. S2. Spatial structure of some MOs with a contribution of AOs of the metals following the results of DFT of calculations: a) HOMO, isoline 0.05; b) LUMO, isoline 0.05; c) HOMO-10, isoline 0.012; d) HOMO-7, isoline 0.02; e)HOMO-5, isoline 0.01; f) HOMO-3, isoline 0.015.

Table S2. Contribution of AOs into the frontier orbitals and some MOs

MO	Energy, eV	Contribution of the main atomic orbitals, %			
		Pd4d	Pb6s	O2p	C2p
LUMO (393)	-2.897344	0	0	17	30
HOMO (392)	-6.475776	23		25	18
HOMO-3 (389)	-6.893296	2	40	14	18
HOMO-5 (387)	-7.018416	15	15	16	22
HOMO-7 (385)	-7.154144	18	13	18	16
HOMO-10 (382)	-7.280624	37	19	11	3
HOMO-13 (379)	-7.61328	2	64	12	5
HOMO-14 (378)	-7.638576	6	65	10	4
HOMO-15 (377)	-7.682368	71	0	7	6
HOMO-16 (376)	-7.70984	71	0	7	6

Kinetic analysis under non-isothermal conditions

Thermogravimetric data were processed with the computer program Netzsch Thermokinetics 2 (Version 2004.05) [1–2]. A special program module, “Model-free”, based on well-known studies [3–13], allows one to process multiple thermogravimetric curves obtained with different heating rates and calculate the activation energy without preliminary information about the kinetic topochemical equation. The Friedman method was used to calculate the activation energies for each experimental point of fractional conversion (in the range $0.005 < \alpha < 0.995$).

We further used the same set of experimental data to search for the corresponding topochemical equation (the selection was made from 16 equations: chemical reaction at the interface, nucleation and diffusion). This calculation was made by the improved differential procedure of Borchardt–Daniels [1, 13] within the multiple linear regression approach. It is very important that the range for the degree of conversion (α) for this calculation is chosen based on the relative constancy of the calculated kinetic parameters from the Friedman analysis.

The *F* test [1] was used to search for the best kinetic description and for statistical control of the obtained equation. It tests the residual variance of individual models against one another and answers the question of whether the models differ significantly (statistically) or not.

The random error in the activation energy values for such a reversible decomposition reaction is usually about 10 % in these experiments, which we took into consideration. The computer program Netzsch Thermokinetics 2 enables estimation of the contribution of each stage (as Δm portion) after this nonlinear regression calculation.

Well-known recommendations for performing kinetic computations on thermal analysis data [14–16] were used; new studies on non-isothermal kinetics were taken into account [17–23].

The kinetic equations to calculate the kinetic parameters are topochemical ones and the calculated parameters (*E* and *A*) are formal and conventional from the standpoint of the classical chemistry of solids.

However, the general trend in the variation of these values within a specially selected series of compounds (either isostructural or genetically related) is very important because the expected disorder in the reaction zones can be identical for them; all other errors will be minimized and smoothed in such a comparison.

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Sublimation and decomposition of *3*

From TG of curves it is visible that process can be divided into three stages: 150–230 ^{o}C (sublimation), 230–260 ^{0}C and 260–280 ^{o}C (heating rate 5 ^{o}/min).

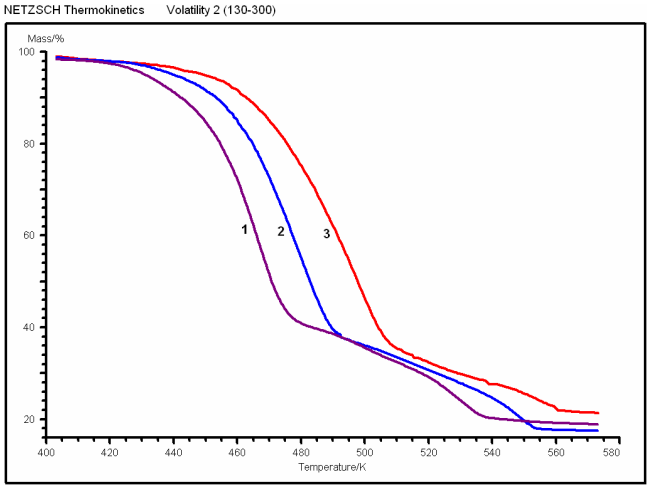

Fig. S3. Sublimation and decomposition of ***3***. TG curves at heating rates of 5 (**1**), 10 (**2**) и 20 (**3**) K min^{-1}.

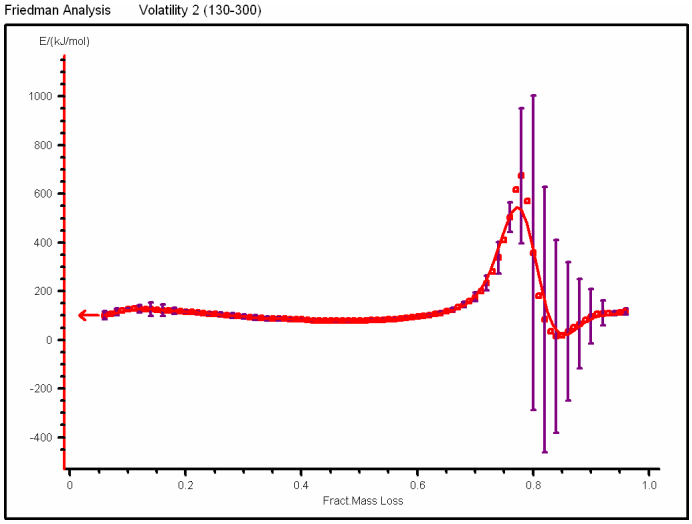

Fig. S4. Sublimation and decomposition of ***3***. The analysis of process by Friedman's method: dependence of the computed value of activation energy on the degree of conversion.

As the curve in Fig. S4 is not monotonous, and activation energy changes, the process can be considered as multistage one, namely, three-stage one.

First stage (sublimation), 0.0–70.0 % of mass loss

TG curves obtained at the three heating rates were used for data processing. The order equations, the equations for surface reaction, the diffusion equations, Arrhenius's equation and the equations of reactions with autocatalysis (Fn, F1, D3, An, C1B, B1) were implemented. Linear regression and nonlinear regression methods were used for the calculations. When comparing the used equations according to F-test and value of the correlation coefficient the best fit gives the order equation (Fig. S5):

A $\rightarrow$ B. Fn, $f_1(\alpha) = (1-\alpha)^{0.69}$, $E_1 = 105 \pm 1$ kJ/mol, lg $A_1 = 9.2 \pm 0.1$

Correlation coefficient 0.998891.

The equation $f_1(\alpha)=(1-\alpha)^{0.69}$ matches the chemical reaction on the surface of a spherical grain ($f(\alpha) = (1-\alpha)^{0.666}$). Apparently, the equation describes the sublimation process.

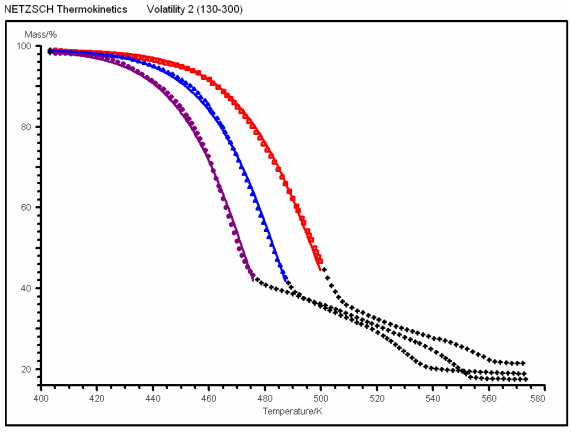

Fig. S5. Sublimation and decomposition of ***3***. Comparison of experimental data (points) and calculated data (lines). Calculation was made following the equation $f_1(\alpha)=(1-\alpha)^{0.69}$ for the first stage of thermolysis (70 % of mass loss).

The second and the third stages (decomposition), 70.0 – 99.9 % of mass loss
The best description is two consecutive reactions (A → B → C), Avrami-Erofeyev's equations:
A → B. An, $f_2(\alpha) = (1-\alpha) / [-\ln(1-\alpha)]^{1.7}$, $E_2 = 105 \pm 7$ kJ/mol, lg $A_2 = 9.7 \pm 0.8$
B → C. An, $f_3(\alpha) = (1-\alpha) \cdot [-\ln(1-\alpha)]^{0.7}$, $E_3 = 78.9 \pm 0.5$ kJ/mol, lg $A_3 = 5.2 \pm 0.1$
Correlation coefficient 0.998891.

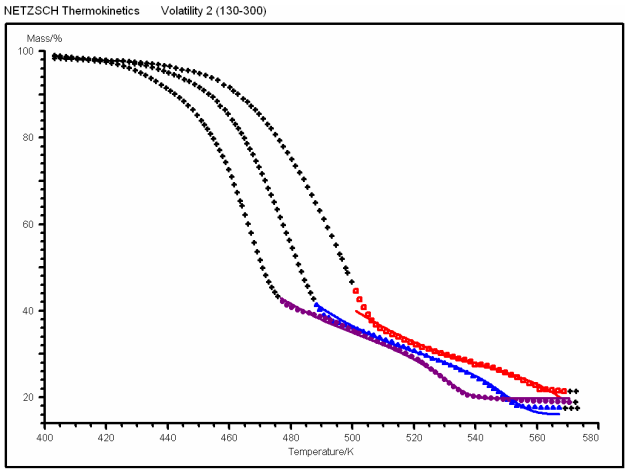

Fig. S6. Sublimation and decomposition of ***3***. Comparison of experimental data (points) and calculated data (lines) for the second or third decomposition stages (70.0 – 99.9 % of mass loss). Calculation was performed for two-stage process both following the equation of Avrami-Yerofeyev (An, An).

Sublimation and decomposition of *5*

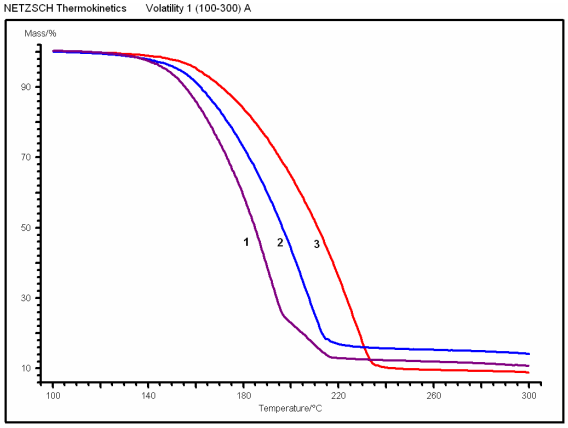

Fig. S7. Sublimation and decomposition of ***5***. TG curves at heating rates of 5 (**1**), 10 (**2**) и 20 (**3**) K min^{-1}.

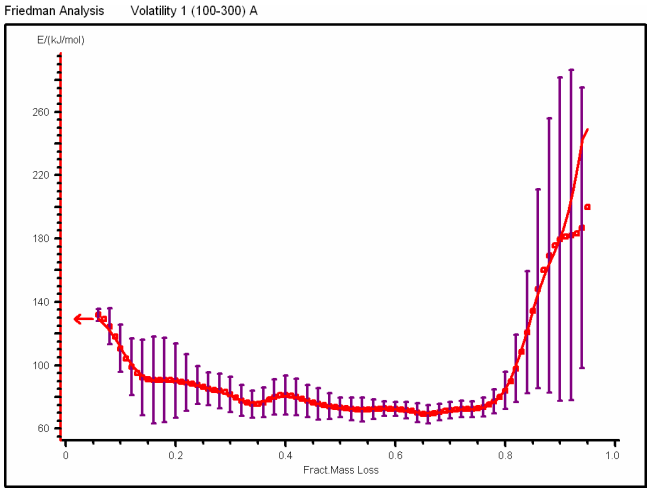

Fig. S8. Sublimation and decomposition of ***3***. The analysis of process by Friedman's method: dependence of the computed value of activation energy on the degree of conversion.

As the curve in Fig. S8 is not monotonous, and activation energy changes, the process can be considered as multistage one, namely, two-stage one.

TG curves obtained at the three heating rates were used for data processing. The order equations, the equations for surface reaction, the diffusion equations, Arrhenius's equation and the equations of reactions with autocatalysis (Fn, F1, D3, An, C1B, B1) were implemented. Linear regression and nonlinear regression methods were used for the calculations. When comparing the used equations according to F-test and value of the correlation coefficient the best fit gives the order equation (Fig. S9):

A $\rightarrow$ B. Fn, $f_2(\alpha) = (1-\alpha)$, E_1 = 92 ± 1 kJ/mol, lg A_1 = 8.1 ± 0.1.

B $\rightarrow$ C. Fn, $f_3(\alpha) = (1-\alpha)^0$, E_2 = 138 ± 10 kJ/mol, lg A_2 = 10.1 ± 0.2.

Correlation coefficient 0.998270.

A $\rightarrow$ B, 97.2% of mass loss,

B $\rightarrow$ C, 2.8% of mass loss.

The first order equation $f_1(\alpha) = (1-\alpha)$ corresponds to nucleation process. Apparently, the equation describes the sublimation process.

The zero order equation $f_1(\alpha) = (1-\alpha)^0$ (constant decomposition rate) corresponds to advance of the reaction zone trough the pressed tablet (decomposition of the cake).

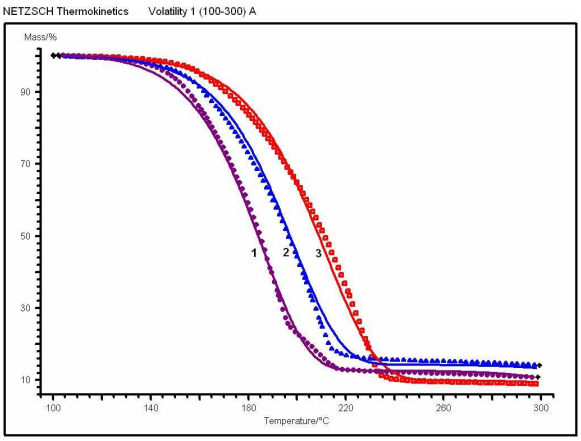

Fig. S9. Sublimation and decomposition of ***5.*** Comparison of experimental data (points) and calculated data (lines) for heating rates of 5 (**1**), 10 (**2**) и 20 (**3**) K min^{-1}. Calculation was performed for two-stage process both following the order equation.

Far-IR spectroscopy

Infrared spectra of the compounds in polyethylene and KBr pellets were recorded using a Vertex 80 FTIR spectrometer.

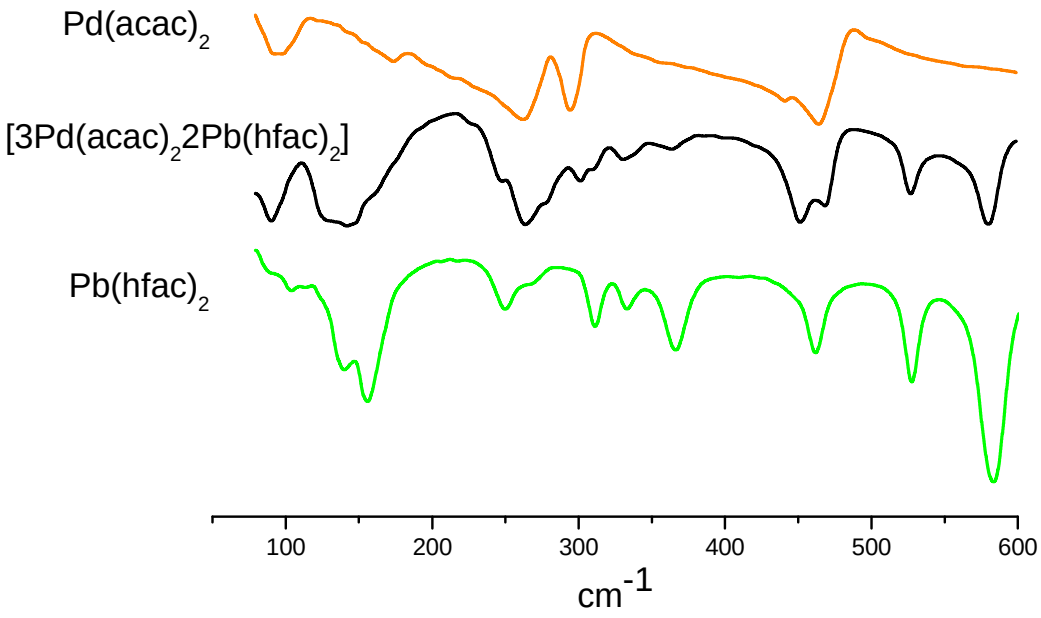

Fig. S10. Experimental infrared spectra for **1**, $Pd(acac)_2$ and $Pb(hfac)_2$

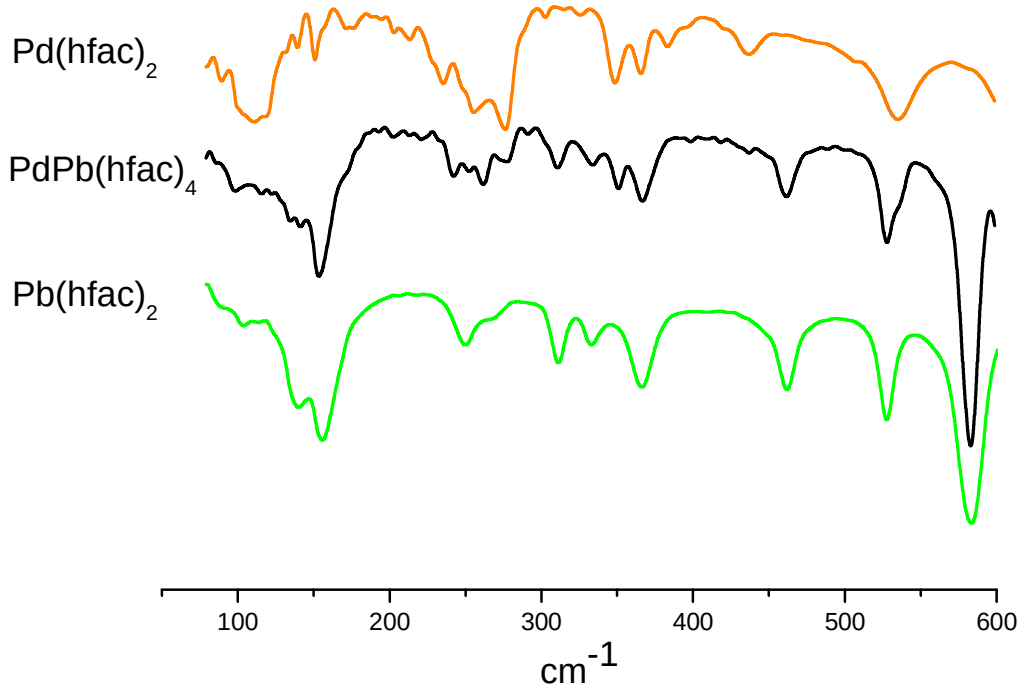

Fig. S11. Experimental infrared spectra for **2**, $Pd(hfa)_2$ and $Pb(hfac)_2$

Annex I
Summary of NBO for 1

Jaguar NBO 5.0

N A T U R A L A T O M I C O R B I T A L A N D
N A T U R A L B O N D O R B I T A L A N A L Y S I S

...

Summary of Natural Population Analysis:

Atom No	Natural Charge	Natural Population			
		Core	Valence	Rydberg	Total
Pb 1	1.50574	78.00000	2.46772	0.02654	80.49426
Pd 2	0.91058	35.99418	9.05932	0.03593	45.08942
Pd 3	0.90943	35.99451	9.06709	0.02897	45.09057
O 4	-0.66082	1.99976	6.65451	0.00655	8.66082
O 5	-0.63754	1.99975	6.63117	0.00662	8.63754
C 6	0.50328	1.99889	3.47458	0.02325	5.49672
C 7	-0.46992	1.99881	4.46052	0.01059	6.46992
H 8	0.25835	0.00000	0.74070	0.00095	0.74165
C 9	0.49341	1.99891	3.48283	0.02485	5.50659
C 10	-0.75704	1.99918	4.75208	0.00578	6.75704
H 11	0.28263	0.00000	0.71467	0.00269	0.71737
H 12	0.25373	0.00000	0.74540	0.00088	0.74627
H 13	0.27788	0.00000	0.71959	0.00253	0.72212
C 14	-0.75634	1.99918	4.75154	0.00561	6.75634
H 15	0.26526	0.00000	0.73377	0.00097	0.73474
H 16	0.26063	0.00000	0.73825	0.00111	0.73937
H 17	0.27815	0.00000	0.71921	0.00265	0.72185
O 18	-0.65724	1.99976	6.65102	0.00646	8.65724
O 19	-0.61622	1.99975	6.60925	0.00722	8.61622
O 20	-0.67594	1.99976	6.66975	0.00642	8.67594
O 21	-0.61335	1.99975	6.60645	0.00715	8.61335
C 22	0.50067	1.99894	3.47491	0.02548	5.49933
C 23	-0.47351	1.99882	4.46435	0.01034	6.47351
H 24	0.25556	0.00000	0.74359	0.00085	0.74444
C 25	0.48893	1.99889	3.48810	0.02407	5.51107
C 26	-0.75015	1.99919	4.74488	0.00607	6.75015
H 27	0.27419	0.00000	0.72424	0.00157	0.72581
H 28	0.24883	0.00000	0.75023	0.00094	0.75117
H 29	0.27722	0.00000	0.72072	0.00206	0.72278
C 30	-0.75225	1.99919	4.74738	0.00568	6.75225
H 31	0.27651	0.00000	0.72115	0.00234	0.72349
H 32	0.24818	0.00000	0.75092	0.00089	0.75182
H 33	0.27291	0.00000	0.72572	0.00137	0.72709
C 34	0.49749	1.99890	3.48095	0.02267	5.50251
C 35	-0.48105	1.99883	4.47209	0.01013	6.48105
H 36	0.25653	0.00000	0.74260	0.00087	0.74347
C 37	0.48999	1.99895	3.48543	0.02563	5.51001
C 38	-0.75799	1.99918	4.75308	0.00572	6.75799
H 39	0.28507	0.00000	0.71212	0.00281	0.71493
H 40	0.24970	0.00000	0.74942	0.00089	0.75030
H 41	0.27849	0.00000	0.71902	0.00249	0.72151
C 42	-0.75259	1.99920	4.74843	0.00496	6.75259
H 43	0.27254	0.00000	0.72569	0.00176	0.72746
H 44	0.25718	0.00000	0.74188	0.00094	0.74282
H 45	0.26562	0.00000	0.73334	0.00103	0.73438
O 46	-0.69692	1.99976	6.68969	0.00746	8.69692
O 47	-0.67373	1.99977	6.66752	0.00644	8.67373
O 48	-0.67490	1.99977	6.66859	0.00654	8.67490
O 49	-0.69865	1.99976	6.69138	0.00751	8.69865
C 50	0.37395	1.99879	3.60393	0.02332	5.62605
C 51	-0.45465	1.99888	4.44193	0.01383	6.45465
H 52	0.28555	0.00000	0.71223	0.00222	0.71445
C 53	0.37955	1.99882	3.59726	0.02437	5.62045
C 54	1.01931	1.99908	2.93165	0.04997	4.98069
C 55	1.01812	1.99908	2.93275	0.05005	4.98188
C 56	0.37752	1.99881	3.59957	0.02409	5.62248
C 57	-0.45484	1.99888	4.44220	0.01376	6.45484
H 58	0.28611	0.00000	0.71166	0.00223	0.71389
C 59	0.37752	1.99880	3.60054	0.02315	5.62248
C 60	1.01834	1.99908	2.93254	0.05004	4.98166
C 61	1.01962	1.99909	2.93134	0.04996	4.98038
F 62	-0.33625	1.99993	7.33439	0.00193	9.33625
F 63	-0.34688	1.99993	7.34541	0.00155	9.34688
F 64	-0.34808	1.99993	7.34627	0.00188	9.34808
F 65	-0.34590	1.99993	7.34409	0.00189	9.34590
F 66	-0.34123	1.99993	7.33939	0.00191	9.34123
F 67	-0.34661	1.99993	7.34510	0.00157	9.34661

F 68	-0.34671	1.99993	7.34491	0.00187	9.34671
F 69	-0.34157	1.99993	7.33974	0.00191	9.34157
F 70	-0.34580	1.99993	7.34431	0.00157	9.34580
F 71	-0.33869	1.99993	7.33683	0.00193	9.33869
F 72	-0.34812	1.99993	7.34662	0.00157	9.34812
F 73	-0.34451	1.99993	7.34268	0.00191	9.34451
Pb 74	1.50802	78.00000	2.46543	0.02656	80.49198
Pd 75	0.90788	35.99464	9.06792	0.02956	45.09212
O 76	-0.65926	1.99976	6.65297	0.00654	8.65926
O 77	-0.63909	1.99975	6.63272	0.00662	8.63909
C 78	0.50455	1.99889	3.47311	0.02345	5.49545
C 79	-0.46912	1.99880	4.45965	0.01066	6.46912
H 80	0.25897	0.00000	0.74003	0.00100	0.74103
C 81	0.49135	1.99891	3.48464	0.02510	5.50865
C 82	-0.75650	1.99918	4.75152	0.00579	6.75650
H 83	0.28137	0.00000	0.71594	0.00269	0.71863
H 84	0.25515	0.00000	0.74394	0.00090	0.74485
H 85	0.27750	0.00000	0.72005	0.00245	0.72250
C 86	-0.75538	1.99918	4.75058	0.00562	6.75538
H 87	0.26472	0.00000	0.73430	0.00097	0.73528
H 88	0.26064	0.00000	0.73824	0.00113	0.73936
H 89	0.27809	0.00000	0.71928	0.00262	0.72191
O 90	-0.65648	1.99976	6.65027	0.00646	8.65648
O 91	-0.61521	1.99974	6.60820	0.00726	8.61521
O 92	-0.67439	1.99976	6.66823	0.00641	8.67439
O 93	-0.61178	1.99975	6.60482	0.00721	8.61178
C 94	0.50017	1.99894	3.47526	0.02562	5.49983
C 95	-0.47367	1.99882	4.46449	0.01037	6.47367
H 96	0.25522	0.00000	0.74392	0.00086	0.74478
C 97	0.48810	1.99889	3.48876	0.02424	5.51190
C 98	-0.75006	1.99919	4.74480	0.00607	6.75006
H 99	0.27463	0.00000	0.72379	0.00157	0.72537
H100	0.24821	0.00000	0.75083	0.00096	0.75179
H101	0.27673	0.00000	0.72123	0.00203	0.72327
C102	-0.75236	1.99919	4.74756	0.00561	6.75236
H103	0.27676	0.00000	0.72092	0.00232	0.72324
H104	0.24810	0.00000	0.75101	0.00089	0.75190
H105	0.27258	0.00000	0.72605	0.00137	0.72742
C106	0.49624	1.99889	3.48207	0.02280	5.50376
C107	-0.48111	1.99883	4.47215	0.01014	6.48111
H108	0.25624	0.00000	0.74289	0.00087	0.74376
C109	0.49057	1.99895	3.48476	0.02572	5.50943
C110	-0.75801	1.99919	4.75310	0.00572	6.75801
H111	0.28429	0.00000	0.71290	0.00281	0.71571
H112	0.24989	0.00000	0.74922	0.00088	0.75011
H113	0.27804	0.00000	0.71949	0.00248	0.72196
C114	-0.75261	1.99920	4.74848	0.00493	6.75261
H115	0.27259	0.00000	0.72565	0.00176	0.72741
H116	0.25721	0.00000	0.74184	0.00094	0.74279
H117	0.26547	0.00000	0.73350	0.00102	0.73453
O118	-0.69695	1.99976	6.68977	0.00742	8.69695
O119	-0.67400	1.99977	6.66783	0.00641	8.67400
O120	-0.67446	1.99977	6.66813	0.00657	8.67446
O121	-0.70133	1.99976	6.69401	0.00756	8.70133
C122	0.37365	1.99879	3.60421	0.02335	5.62635
C123	-0.45429	1.99888	4.44155	0.01386	6.45429
H124	0.28566	0.00000	0.71212	0.00222	0.71434
C125	0.37995	1.99882	3.59688	0.02435	5.62005
C126	1.01940	1.99908	2.93153	0.04999	4.98060
C127	1.01804	1.99908	2.93285	0.05002	4.98196
C128	0.37847	1.99882	3.59859	0.02412	5.62153
C129	-0.45443	1.99888	4.44179	0.01376	6.45443
H130	0.28633	0.00000	0.71144	0.00223	0.71367
C131	0.37759	1.99879	3.60048	0.02313	5.62241
C132	1.01835	1.99909	2.93253	0.05003	4.98165
C133	1.01973	1.99909	2.93122	0.04996	4.98027
F134	-0.33635	1.99993	7.33450	0.00193	9.33635
F135	-0.34712	1.99993	7.34564	0.00155	9.34712
F136	-0.34788	1.99993	7.34607	0.00188	9.34788
F137	-0.34593	1.99993	7.34411	0.00188	9.34593
F138	-0.34138	1.99993	7.33954	0.00191	9.34138
F139	-0.34631	1.99993	7.34481	0.00157	9.34631
F140	-0.34168	1.99993	7.33985	0.00191	9.34168
F141	-0.34654	1.99993	7.34473	0.00188	9.34654
F142	-0.34591	1.99993	7.34441	0.00157	9.34591
F143	-0.33900	1.99993	7.33714	0.00193	9.33900
F144	-0.34796	1.99993	7.34646	0.00157	9.34796
F145	-0.34418	1.99993	7.34234	0.00191	9.34418
* Total *	0.00000	451.92556	570.60527	1.46917	*********

Natural Population

Effective Core	240.00000	
Core	211.92556	(99.9649% of 212)
Valence	570.60527	(99.7562% of 572)
Natural Minimal Basis	1022.53083	(99.8565% of1024)
Natural Rydberg Basis	1.46917	(0.1435% of1024)

Atom No	Natural Electron Configuration
Pb 1	[core]6s(1.95)6p(0.52)7p(0.03)
Pd 2	[core]5s(0.35)4d(8.71)5p(0.02)5d(0.01)6p(0.01)
Pd 3	[core]5s(0.36)4d(8.71)5d(0.01)6p(0.02)

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
within unit 1				
263. LP (1)Pb 1	393. LP*(2)Pb 1	0.74	0.48	0.018
from unit 1 to unit 2				
263. LP (1)Pb 1	873. BD*(1)Pd 2- O 4	0.19	0.39	0.008
263. LP (1)Pb 1	874. BD*(1)Pd 2- O 5	0.18	0.39	0.008
263. LP (1)Pb 1	877. BD*(1) O 4- C 6	0.35	0.80	0.015
263. LP (1)Pb 1	878. BD*(2) O 4- C 6	0.14	0.36	0.007
from unit 1 to unit 3				
263. LP (1)Pb 1	875. BD*(1)Pd 3- O18	0.09	0.39	0.006
263. LP (1)Pb 1	876. BD*(1)Pd 3- O19	0.14	0.39	0.007
263. LP (1)Pb 1	892. BD*(1) O18- C25	0.35	0.80	0.015
263. LP (1)Pb 1	893. BD*(2) O18- C25	0.13	0.36	0.007
from unit 2 to unit 1				
1. BD (1)Pd 2- O 4	393. LP*(2)Pb 1	2.54	0.56	0.035
1. BD (1)Pd 2- O 4	394. LP*(3)Pb 1	0.44	0.52	0.014
1. BD (1)Pd 2- O 4	395. LP*(4)Pb 1	0.79	0.57	0.019
1. BD (1)Pd 2- O 4	399. RY*(1)Pb 1	0.47	1.03	0.020
1. BD (1)Pd 2- O 4	400. RY*(2)Pb 1	0.30	0.99	0.016
1. BD (1)Pd 2- O 4	401. RY*(3)Pb 1	0.20	0.90	0.012
2. BD (1)Pd 2- O 5	393. LP*(2)Pb 1	0.21	0.56	0.010
2. BD (1)Pd 2- O 5	395. LP*(4)Pb 1	0.07	0.58	0.006
2. BD (1)Pd 2- O 5	399. RY*(1)Pb 1	0.08	1.03	0.008
5. BD (1) O 4- C 6	393. LP*(2)Pb 1	0.55	1.06	0.023
5. BD (1) O 4- C 6	394. LP*(3)Pb 1	0.58	1.02	0.023
5. BD (1) O 4- C 6	395. LP*(4)Pb 1	0.75	1.08	0.026
5. BD (1) O 4- C 6	399. RY*(1)Pb 1	0.06	1.53	0.009
5. BD (1) O 4- C 6	400. RY*(2)Pb 1	0.08	1.49	0.010
5. BD (1) O 4- C 6	401. RY*(3)Pb 1	0.12	1.40	0.012
6. BD (2) O 4- C 6	393. LP*(2)Pb 1	0.46	0.45	0.013
6. BD (2) O 4- C 6	395. LP*(4)Pb 1	1.15	0.46	0.021
9. BD (1) C 6- C 7	393. LP*(2)Pb 1	0.09	0.80	0.008
9. BD (1) C 6- C 7	394. LP*(3)Pb 1	0.18	0.75	0.011
9. BD (1) C 6- C 7	395. LP*(4)Pb 1	0.42	0.81	0.017
10. BD (1) C 6- C10	393. LP*(2)Pb 1	0.07	0.71	0.006
10. BD (1) C 6- C10	395. LP*(4)Pb 1	0.06	0.72	0.006
14. BD (1) C10- H11	395. LP*(4)Pb 1	0.33	0.58	0.013
16. BD (1) C10- H13	394. LP*(3)Pb 1	0.13	0.52	0.008
16. BD (1) C10- H13	395. LP*(4)Pb 1	0.09	0.58	0.007
157. CR (1)Pd 2	393. LP*(2)Pb 1	1.35	3.43	0.064
157. CR (1)Pd 2	394. LP*(3)Pb 1	0.30	3.39	0.030
157. CR (1)Pd 2	395. LP*(4)Pb 1	0.18	3.44	0.023
157. CR (1)Pd 2	399. RY*(1)Pb 1	0.22	3.90	0.026
157. CR (1)Pd 2	401. RY*(3)Pb 1	0.08	3.77	0.015
158. CR (2)Pd 2	393. LP*(2)Pb 1	0.14	2.15	0.016
160. CR (4)Pd 2	393. LP*(2)Pb 1	0.21	2.18	0.020
160. CR (4)Pd 2	394. LP*(3)Pb 1	0.07	2.13	0.011
165. CR (1) O 4	393. LP*(2)Pb 1	0.39	19.02	0.080
165. CR (1) O 4	394. LP*(3)Pb 1	0.44	18.98	0.085
165. CR (1) O 4	395. LP*(4)Pb 1	0.73	19.03	0.109
165. CR (1) O 4	399. RY*(1)Pb 1	0.05	19.49	0.028
165. CR (1) O 4	400. RY*(2)Pb 1	0.11	19.45	0.040
165. CR (1) O 4	401. RY*(3)Pb 1	0.07	19.36	0.032
167. CR (1) C 6	395. LP*(4)Pb 1	0.16	10.24	0.038

266. LP (3)Pd 2	393. LP*(2)Pb 1	0.32	0.35	0.010
266. LP (3)Pd 2	399. RY*(1)Pb 1	0.15	0.82	0.010
267. LP (4)Pd 2	393. LP*(2)Pb 1	0.07	0.36	0.005
272. LP (1) O 4	393. LP*(2)Pb 1	2.79	0.69	0.040
272. LP (1) O 4	394. LP*(3)Pb 1	5.25	0.65	0.053
272. LP (1) O 4	395. LP*(4)Pb 1	6.50	0.70	0.062
272. LP (1) O 4	399. RY*(1)Pb 1	0.16	1.16	0.012
272. LP (1) O 4	400. RY*(2)Pb 1	0.35	1.12	0.018
272. LP (1) O 4	401. RY*(3)Pb 1	0.33	1.03	0.017

from unit 3 to unit 1

3. BD (1)Pd 3- O18	393. LP*(2)Pb 1	3.50	0.56	0.041
3. BD (1)Pd 3- O18	394. LP*(3)Pb 1	0.85	0.52	0.019
3. BD (1)Pd 3- O18	395. LP*(4)Pb 1	0.09	0.57	0.007
3. BD (1)Pd 3- O18	399. RY*(1)Pb 1	0.89	1.03	0.027
3. BD (1)Pd 3- O18	401. RY*(3)Pb 1	0.12	0.90	0.009
4. BD (1)Pd 3- O19	393. LP*(2)Pb 1	0.31	0.55	0.012
4. BD (1)Pd 3- O19	394. LP*(3)Pb 1	0.09	0.51	0.006
4. BD (1)Pd 3- O19	399. RY*(1)Pb 1	0.15	1.02	0.011
20. BD (1) O18- C25	393. LP*(2)Pb 1	0.96	1.06	0.030
20. BD (1) O18- C25	394. LP*(3)Pb 1	0.60	1.02	0.023
20. BD (1) O18- C25	399. RY*(1)Pb 1	0.14	1.54	0.013
20. BD (1) O18- C25	401. RY*(3)Pb 1	0.08	1.40	0.009
21. BD (2) O18- C25	393. LP*(2)Pb 1	0.85	0.45	0.018
21. BD (2) O18- C25	395. LP*(4)Pb 1	0.20	0.46	0.009
31. BD (1) C23- C25	393. LP*(2)Pb 1	0.31	0.80	0.015
31. BD (1) C23- C25	394. LP*(3)Pb 1	0.20	0.76	0.011
31. BD (1) C23- C25	395. LP*(4)Pb 1	0.07	0.81	0.007
31. BD (1) C23- C25	399. RY*(1)Pb 1	0.05	1.27	0.007
35. BD (1) C26- H29	394. LP*(3)Pb 1	0.06	0.53	0.005
35. BD (1) C26- H29	395. LP*(4)Pb 1	0.23	0.59	0.011
161. CR (1)Pd 3	393. LP*(2)Pb 1	2.00	3.43	0.077
161. CR (1)Pd 3	394. LP*(3)Pb 1	0.53	3.39	0.039
161. CR (1)Pd 3	395. LP*(4)Pb 1	0.27	3.44	0.028
161. CR (1)Pd 3	399. RY*(1)Pb 1	0.37	3.90	0.034
162. CR (2)Pd 3	393. LP*(2)Pb 1	0.22	2.14	0.020
162. CR (2)Pd 3	399. RY*(1)Pb 1	0.05	2.62	0.010
163. CR (3)Pd 3	393. LP*(2)Pb 1	0.22	2.17	0.021
163. CR (3)Pd 3	394. LP*(3)Pb 1	0.09	2.13	0.013
164. CR (4)Pd 3	393. LP*(2)Pb 1	0.06	2.17	0.011
164. CR (4)Pd 3	395. LP*(4)Pb 1	0.07	2.19	0.011
172. CR (1) O18	393. LP*(2)Pb 1	0.78	19.02	0.114
172. CR (1) O18	394. LP*(3)Pb 1	0.52	18.97	0.093
172. CR (1) O18	395. LP*(4)Pb 1	0.07	19.03	0.035
172. CR (1) O18	399. RY*(1)Pb 1	0.15	19.49	0.049
172. CR (1) O18	401. RY*(3)Pb 1	0.07	19.35	0.032
178. CR (1) C25	393. LP*(2)Pb 1	0.09	10.23	0.029
178. CR (1) C25	394. LP*(3)Pb 1	0.05	10.18	0.022
270. LP (3)Pd 3	393. LP*(2)Pb 1	0.40	0.34	0.011
270. LP (3)Pd 3	395. LP*(4)Pb 1	0.05	0.36	0.004
270. LP (3)Pd 3	399. RY*(1)Pb 1	0.19	0.82	0.011
271. LP (4)Pd 3	393. LP*(2)Pb 1	0.09	0.36	0.005
275. LP (1) O18	393. LP*(2)Pb 1	6.40	0.68	0.061
275. LP (1) O18	394. LP*(3)Pb 1	6.41	0.64	0.059
275. LP (1) O18	395. LP*(4)Pb 1	0.81	0.70	0.022
275. LP (1) O18	399. RY*(1)Pb 1	0.55	1.16	0.023
275. LP (1) O18	401. RY*(3)Pb 1	0.37	1.02	0.018

from unit 3 to unit 2

3. BD (1)Pd 3- O18	873. BD*(1)Pd 2- O 4	0.05	0.47	0.005
21. BD (2) O18- C25	404. RY*(1)Pd 2	0.07	0.70	0.006
21. BD (2) O18- C25	873. BD*(1)Pd 2- O 4	0.12	0.35	0.006
21. BD (2) O18- C25	874. BD*(1)Pd 2- O 5	0.11	0.35	0.006
28. BD (1) C22- C23	409. RY*(6)Pd 2	0.06	1.57	0.009
31. BD (1) C23- C25	404. RY*(1)Pd 2	0.05	1.05	0.007
31. BD (1) C23- C25	409. RY*(6)Pd 2	0.07	1.57	0.009
270. LP (3)Pd 3	873. BD*(1)Pd 2- O 4	0.07	0.25	0.004
270. LP (3)Pd 3	874. BD*(1)Pd 2- O 5	0.08	0.25	0.004

from unit 4 to unit 1

24. BD (1) O20- C34	393. LP*(2)Pb 1	0.64	1.07	0.025
24. BD (1) O20- C34	394. LP*(3)Pb 1	0.70	1.03	0.025
24. BD (1) O20- C34	395. LP*(4)Pb 1	1.00	1.09	0.030
24. BD (1) O20- C34	399. RY*(1)Pb 1	0.11	1.54	0.012
24. BD (1) O20- C34	400. RY*(2)Pb 1	0.09	1.50	0.011
24. BD (1) O20- C34	401. RY*(3)Pb 1	0.07	1.41	0.009
25. BD (2) O20- C34	393. LP*(2)Pb 1	0.33	0.45	0.011
25. BD (2) O20- C34	394. LP*(3)Pb 1	0.08	0.41	0.005
25. BD (2) O20- C34	395. LP*(4)Pb 1	0.94	0.46	0.019
39. BD (1) C34- C35	393. LP*(2)Pb 1	0.08	0.80	0.008

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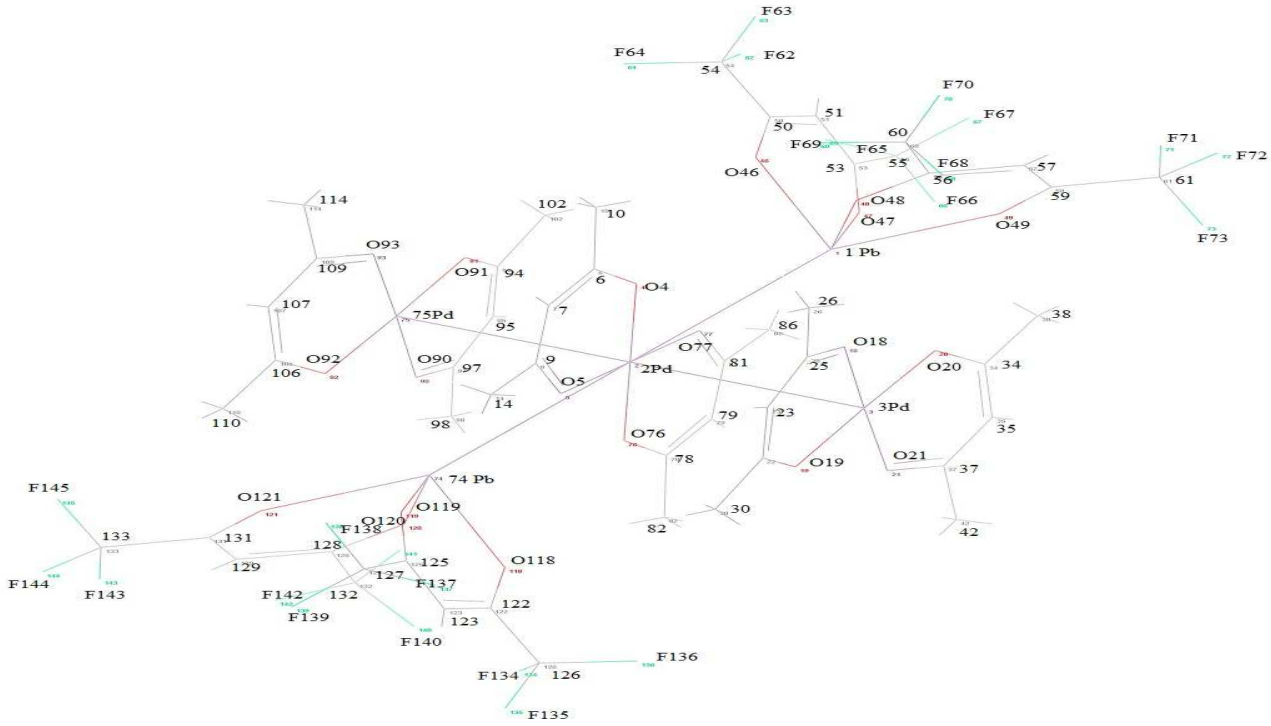
  39. BD ( 1) C34- C35      394. LP*( 3)Pb 1             0.21    0.76    0.012
  39. BD ( 1) C34- C35      395. LP*( 4)Pb 1             0.46    0.81    0.018
  40. BD ( 1) C34- C38      393. LP*( 2)Pb 1             0.07    0.71    0.007
  40. BD ( 1) C34- C38      395. LP*( 4)Pb 1             0.05    0.73    0.006
  44. BD ( 1) C38- H39      395. LP*( 4)Pb 1             0.26    0.58    0.011
  46. BD ( 1) C38- H41      394. LP*( 3)Pb 1             0.12    0.52    0.007
  46. BD ( 1) C38- H41      395. LP*( 4)Pb 1             0.08    0.58    0.006
 174. CR ( 1) O20           393. LP*( 2)Pb 1             0.40   19.02    0.082
 174. CR ( 1) O20           394. LP*( 3)Pb 1             0.55   18.98    0.095
 174. CR ( 1) O20           395. LP*( 4)Pb 1             0.96   19.03    0.125
 174. CR ( 1) O20           399. RY*( 1)Pb 1             0.08   19.49    0.036
 174. CR ( 1) O20           400. RY*( 2)Pb 1             0.12   19.45    0.044
 181. CR ( 1) C34           394. LP*( 3)Pb 1             0.06   10.19    0.023
 181. CR ( 1) C34           395. LP*( 4)Pb 1             0.17   10.24    0.039
 277. LP ( 1) O20           393. LP*( 2)Pb 1             2.73    0.69    0.040
 277. LP ( 1) O20           394. LP*( 3)Pb 1             6.27    0.65    0.058
 277. LP ( 1) O20           395. LP*( 4)Pb 1             8.82    0.70    0.072
 277. LP ( 1) O20           399. RY*( 1)Pb 1             0.26    1.16    0.016
 277. LP ( 1) O20           400. RY*( 2)Pb 1             0.35    1.12    0.018
 277. LP ( 1) O20           401. RY*( 3)Pb 1             0.17    1.03    0.012
 277. LP ( 1) O20           403. RY*( 5)Pb 1             0.05   10.40    0.021
 278. LP ( 2) O20           393. LP*( 2)Pb 1             2.18    0.48    0.030
 278. LP ( 2) O20           394. LP*( 3)Pb 1             0.50    0.44    0.014
 278. LP ( 2) O20           395. LP*( 4)Pb 1             0.61    0.49    0.016
 278. LP ( 2) O20           399. RY*( 1)Pb 1             0.24    0.95    0.015
 278. LP ( 2) O20           400. RY*( 2)Pb 1             0.20    0.91    0.013
 278. LP ( 2) O20           401. RY*( 3)Pb 1             0.08    0.82    0.008
...
NATURAL BOND ORBITAL ANALYSIS, alpha spin orbitals:
     (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 --------------------------------------------------------------------------------
   1. (1.93588) BD ( 1)Pd  2- O  4
                ( 14.37%)   0.3791*Pd  2 s( 47.45%)p 0.01(  0.45%)d 1.10( 52.10%)
                ( 85.63%)   0.9254* O  4 s( 12.37%)p 7.08( 87.63%)
   3. (1.93608) BD ( 1)Pd  3- O 18
                ( 14.55%)   0.3815*Pd  3 s( 47.61%)p 0.01(  0.49%)d 1.09( 51.90%)
                ( 85.45%)   0.9244* O 18 s( 12.73%)p 6.85( 87.27%)
   6. (1.97885) BD ( 2) O  4- C  6
                ( 79.38%)   0.8910* O  4 s(  0.11%)p99.99( 99.89%)
                ( 20.62%)   0.4541* C  6 s(  0.01%)p99.99( 99.99%)
...
157. (1.99720) CR ( 1)Pd  2            s(100.00%)p 0.00(  0.00%)d 0.00(  0.00%)
...
161. (1.99751) CR ( 1)Pd  3            s(100.00%)p 0.00(  0.00%)d 0.00(  0.00%)
263. (1.97806) LP ( 1)Pb  1            s( 98.53%)p 0.01(  1.47%)
...
272. (1.93790) LP ( 1) O  4            s( 48.99%)p 1.04( 51.01%)
...
275. (1.94032) LP ( 1) O 18            s( 48.44%)p 1.06( 51.56%)
277. (1.93418) LP ( 1) O 20            s( 48.42%)p 1.07( 51.58%)
278. (1.70999) LP ( 2) O 20            s( 10.66%)p 8.38( 89.34%)
...
393. (0.18092) LP*( 2)Pb  1            s(  1.53%)p64.39( 98.47%)
394. (0.16275) LP*( 3)Pb  1            s(  0.00%)p 1.00(100.00%)
395. (0.14827) LP*( 4)Pb  1            s(  0.00%)p 1.00(100.00%)
...
873. (0.33540) BD*( 1)Pd  2- O  4
                ( 85.63%)   0.9254*Pd  2 s( 47.45%)p 0.01(  0.45%)d 1.10( 52.10%)
                ( 14.37%)  -0.3791* O  4 s( 12.37%)p 7.08( 87.63%)
874. (0.33486) BD*( 1)Pd  2- O  5
                ( 85.56%)   0.9250*Pd  2 s( 47.05%)p 0.01(  0.45%)d 1.12( 52.50%)
                ( 14.44%)  -0.3799* O  5 s( 12.40%)p 7.07( 87.60%)
875. (0.33270) BD*( 1)Pd  3- O 18
                ( 85.45%)   0.9244*Pd  3 s( 47.61%)p 0.01(  0.49%)d 1.09( 51.90%)
                ( 14.55%)  -0.3815* O 18 s( 12.73%)p 6.85( 87.27%)
876. (0.32379) BD*( 1)Pd  3- O 19
                ( 84.54%)   0.9195*Pd  3 s( 46.52%)p 0.01(  0.58%)d 1.14( 52.90%)
                ( 15.46%)  -0.3931* O 19 s( 11.59%)p 7.63( 88.41%)
877. (0.02730) BD*( 1) O  4- C  6
                ( 33.09%)   0.5753* O  4 s( 38.54%)p 1.59( 61.46%)
                ( 66.91%)  -0.8180* C  6 s( 25.89%)p 2.86( 74.11%)
878. (0.47261) BD*( 2) O  4- C  6
                ( 20.62%)   0.4541* O  4 s(  0.11%)p99.99( 99.89%)
                ( 79.38%)  -0.8910* C  6 s(  0.01%)p99.99( 99.99%)
892. (0.02833) BD*( 1) O 18- C 25
                ( 33.14%)   0.5757* O 18 s( 38.83%)p 1.58( 61.17%)
                ( 66.86%)  -0.8177* C 25 s( 25.84%)p 2.87( 74.16%)
896. (0.03219) BD*( 1) O 20- C 34
                ( 67.11%)  -0.8192* C 34 s( 25.74%)p 2.88( 74.26%)
                (32.89%)   0.5735* O 20 s( 40.87%)p 1.45( 59.13%)
```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