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- Supplementary Information -

Synthesis and Structure of $[U\{C(PPh_2NMes)_2\}_2]$ (Mes = 2,4,6-$Me_3C_6H_2$): A Homoleptic Uranium Bis(Carbene) Complex with two U=C Double Bonds

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Experimental

General

All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors. Deuterated solvent was distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. $H_2C(PPh_2NMes)_2$[1] and $[UI_3(THF)_4]$,[2] were prepared according to published procedures. Bu^tLi was purchased as a 1.0 M solution in pentane, pumped down to dryness, and stored in the glovebox.

^{1}H, ^{13}C, and ^{7}Li NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, and 155.5 MHz respectively; chemical shifts are quoted in ppm and are relative to TMS or external 1M LiCl. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental microanalyses for **2** was carried out by Mr Stephen Boyer (London Metropolitan University). The yield of **3** was not optimised.

Synthesis of [Li$_2${C(PPh$_2$NMes)$_2$}$_2$]$_2$ (2)

Toluene (30 ml) was added to a pre-cooled (–78 °C) mixture of $H_2C(PPh_2NMes)_2$ (6.51 g, 10 mmol) and solid Bu^{t}Li (1.28 g, 20 mmol). The mixture was allowed to warm slowly to room temperature with stirring over 18 hours to afford a yellow solution. Volatiles were removed *in vacuo* and the resulting pale yellow solid was washed with hexane to afford **2** as white powder. Yield: 5.7 g, 86%. Colourless crystals were obtained from a saturated solution in toluene (10 ml). Anal Calcd for $C_{43}H_{42}N_2P_2Li_2$: C, 79.61; H, 6.63; N, 4.32. Found: C, 79.55; H, 6.52; N, 4.28. ^{1}H NMR (C_6D_6, 298 K): δ 2.09 (s, 24H, *ortho*-CH_3) 2.34 (s, 12H, *para*-CH_3), 6.83 (t, $^{2}J_{HH}$ = 7.50 Hz, 16H, *meta*-C*H*), 6.92 (s, 8H, *meta*-Mes), 6.99 (t, $^{3}J_{HH}$ = 7.50 Hz, 8H, *para*-C*H*), 7.62 (dd, $^{3}J_{HH}$ = 7.50 Hz, $^{3}J_{PH}$ = 10.80 Hz, 16H, *ortho*-Ph). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): 20.59 (*para*-Me), 22.12 (*ortho*-Me), 125.46 (*ipso*-Mes), 126.98 (*ortho*-Ph), 128.79 (*ortho*-Mes), 129.84 (*para*-Ph), 132.26 (*ortho*-Ph), 134.73 (*meta*-Mes), 140.10 (virtual t, J_{CP} = 38.24 Hz, *ipso*-Ph), 146.14 (*para*-Mes). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ 16.94 (s). ^{7}Li{^{1}H} NMR (C_6D_6, 298 K): δ 4.32 (s). FTIR ν/cm^{-1} (Nujol): 1261 (s), 1235 (s), 1134 (br, m), 1097 (s), 1023 (s).

Synthesis of [U{C(PPh$_2$NMes)$_2$}$_2$] (3)

A mixture of toluene (20 ml) and diethyl ether (20 ml) was added to a pre-cooled (–78 °C) mixture of **2** (1.33 g, 2 mmol) and [$UI_3(THF)_4$] (1.82 g, 2 mmol). The mixture was allowed to slowly warm to room temperature with stirring over 88 hours to afford a deep blue solution. Volatiles were removed *in vacuo* and the resulting deep blue solid was recrystallised from toluene (10 ml) to afford **3** as yellow crystals. Yield: 0.46 g, 24%. Anal Calcd for $C_{114}H_{116}N_4P_4U_2$: C, 71.91; H, 6.14; N, 2.94. Found: C, 69.23; H, 5.77; N, 2.27. ^{1}H NMR (C_6D_6, 298 K): δ –38.28 (s, v br, 16H), –6.38 (s, br, 4H), –3.61 (s , br, 12H), 2.60 (s, br, 4H), 7.11 (s, br, 12H), 10.89 (s, br, 8H), 12.20 (s, br, 12H), 29.77 (s, v br, 16H). IR ν/cm^{-1} (Nujol): 1306 (s), 1238 (s), 1192 (br, m), 1148 (s), 1101 (s). μ_{eff} (Evans method, C_6D_6, 298 K): 2.61 μ_B.

Computational Details

General

Unrestricted geometry optimizations were performed for a model of **3** using coordinates derived from the X-ray crystal structure of **3**. No constraints were imposed on the structures during the geometry optimizations. The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2009.01.[3,4] The DFT geometry optimizations employed Slater type orbital (STO) triple-ζ-plus polarization basis sets (from the ZORA/TZP database of the ADF suite). The cores for C, N, P and U were frozen up to 1s for C and N, 2p for P, and 5d for U. Scalar relativistic approaches were used within the ZORA Hamiltonian for the inclusion of relativistic effects and the local density approximation (LDA) with the correlation

potential due to Vosko et al.[5] was used in all of the calculations. Gradient corrections were performed using the functionals of Becke[6] and Perdew.[7] The program MOLEKEL[8] was used to prepare the three-dimensional plot of the electron density.

Geometry Optimised Coordinates and Final Energy for 3

1.H	1.778173	3.217473	-7.629433
2.H	0.166731	3.852929	-7.238771
3.H	-2.041191	-0.035121	-7.470320
4.C	1.198368	3.753650	-6.866839
5.H	1.607620	4.772223	-6.787547
6.H	-2.685163	-2.283169	-6.592945
7.C	-2.098331	-0.207642	-6.393484
8.H	2.381444	1.356570	-6.251422
9.H	-1.532117	1.815160	-5.871675
10.C	-2.459418	-1.468659	-5.902383
11.C	1.245441	3.036651	-5.536966
12.C	-1.818742	0.830258	-5.501221
13.C	1.901609	1.817419	-5.382847
14.H	2.444107	-0.754198	-5.056589
15.H	0.068375	4.508190	-4.479705
16.C	0.614642	3.563268	-4.403631
17.C	-2.547950	-1.685561	-4.526468
18.H	0.108686	-2.734898	-4.523665
19.H	-2.853098	-2.666622	-4.159394
20.C	-1.893888	0.610786	-4.121486
21.C	1.971906	1.135510	-4.154832
22.C	2.695455	-0.184786	-4.151301
23.H	1.587495	-2.986600	-3.582969
24.H	0.531985	-5.369124	-3.711318
25.H	3.787553	-0.045920	-4.137541
26.H	-0.063606	-7.674694	-3.306812
27.C	0.524184	-2.718061	-3.505762
28.C	-2.257244	-0.646663	-3.621619
29.H	-1.668414	1.415612	-3.421640
30.C	0.665020	2.929369	-3.158842
31.H	0.448857	-1.689100	-3.143161
32.H	2.430548	-0.781710	-3.278256
33.C	-0.050983	-5.055937	-2.839344
34.C	1.374300	1.705379	-3.002593
35.H	4.388079	5.651217	-2.556431
36.H	-4.245626	4.729364	-2.910962
37.C	-0.444605	-7.502168	-2.291868
38.C	-0.189370	-3.679073	-2.593609
39.H	3.560374	3.330607	-2.765562
40.H	-0.639860	4.418301	-2.317319

41.H	-1.395557	-8.044460	-2.189259
42.H	7.221986	-1.815847	-2.551569
43.H	7.460474	0.659585	-2.367838
44.H	0.266023	-7.962611	-1.587360
45.C	-0.616721	-6.026479	-2.013032
46.C	-0.016782	3.575590	-1.993037
47.C	6.387457	-1.209197	-2.196116
48.C	6.520796	0.177301	-2.093591
49.H	-3.347640	2.523442	-2.160163
50.C	4.150255	5.082169	-1.656403
51.H	-7.305526	-0.483365	-1.962594
52.H	-4.977601	0.332291	-1.760799
53.C	3.679439	3.771494	-1.774723
54.C	-4.097972	4.533922	-1.847480
55.C	-5.171173	-0.740082	-1.818106
56.C	-6.483548	-1.200006	-1.935650
57.P	-2.397827	-0.912686	-1.803581
58.H	5.069423	-2.901541	-1.901236
59.H	-0.655178	2.858138	-1.459608
60.C	5.180522	-1.818558	-1.831813
61.C	-4.096128	-1.644810	-1.780166
62.C	5.452451	0.958001	-1.637180
63.C	-6.740618	-2.572423	-2.021408
64.H	5.575570	2.038444	-1.556295
65.H	-7.767029	-2.933217	-2.111676
66.N	1.444562	1.090926	-1.695384
67.C	-4.360193	-3.020111	-1.888140
68.H	-3.543013	-3.741062	-1.894805
69.C	-5.677091	-3.478366	-1.999812
70.C	-0.953306	-3.244360	-1.484994
71.H	0.718226	3.953806	-1.271574
72.C	-3.602086	3.294743	-1.431670
73.H	-5.866678	-4.550222	-2.079179
74.H	-4.778477	6.490057	-1.223367
75.C	4.117900	-1.040360	-1.378806
76.C	4.233728	0.356890	-1.284130
77.N	-1.165474	-1.855150	-1.197056
78.C	-1.319472	-5.579536	-0.885177
79.C	-2.150432	0.532154	-0.949367
80.C	-4.397236	5.519200	-0.901398
81.H	3.178157	-1.518051	-1.100800
82.H	4.691102	6.684196	-0.306551
83.C	4.319406	5.661511	-0.393591
84.C	3.359105	3.029829	-0.621840
85.C	-1.486327	-4.221995	-0.597887
86.P	2.757143	1.289147	-0.684274
87.H	1.704671	-3.324340	-0.580420
88.H	-1.747728	-6.312032	-0.194926
89.H	2.612137	-4.803317	-0.207520
90.C	-3.408360	3.022352	-0.068424

91.C	2.327791	-3.816703	0.179484
92.H	3.241105	-3.219869	0.298813
93.U	0.000926	-0.016276	0.002089
94.P	-2.785483	1.348541	0.389305
95.C	-4.206602	5.257071	0.460088
96.C	4.012010	4.926635	0.755719
97.H	-0.779269	4.149740	0.446286
98.H	-3.182929	-3.326515	0.411195
99.C	3.530713	3.619206	0.640093
100.C	-2.230924	-3.820344	0.647652
101.H	-5.591613	2.261812	1.127136
102.C	-3.722586	4.014532	0.879558
103.H	0.595974	3.123698	0.867546
104.C	2.139362	0.780548	0.806470
105.H	-4.437598	6.022165	1.202837
106.C	-4.256607	0.553420	1.171916
107.C	-5.469273	1.217621	1.416178
108.H	-2.445698	-4.699538	1.268384
109.C	-0.056740	3.924674	1.240635
110.H	-1.634451	-3.120855	1.249398
111.H	4.143433	5.370975	1.743895
112.H	0.554564	4.820575	1.406403
113.H	-3.206996	-1.326587	1.345474
114.H	1.865346	-6.082006	1.524246
115.C	1.577329	-3.955174	1.477735
116.H	3.273711	3.038330	1.527188
117.C	-4.141949	-0.799143	1.536470
118.H	7.830596	-2.213847	2.692015
119.N	-1.478151	1.397538	1.425348
120.H	7.313807	0.131930	2.010497
121.N	1.213654	-1.522265	1.563086
122.C	6.508523	-0.592466	2.140670
123.C	-6.532681	0.546410	2.030933
124.C	6.796672	-1.906442	2.524389
125.H	4.967485	0.828808	1.637457
126.H	-7.467244	1.077635	2.218393
127.C	5.186392	-0.200665	1.925891
128.H	-3.585971	3.823507	1.944940
129.C	1.422215	-5.226797	2.042069
130.C	5.754786	-2.820883	2.700629
131.H	5.969159	-3.844601	3.012309
132.C	-5.200022	-1.468458	2.146779
133.C	4.133291	-1.117780	2.086236
134.P	2.418145	-0.440085	1.952004
135.C	-6.400300	-0.793626	2.401328
136.C	4.428371	-2.430167	2.490425
137.C	1.025467	-2.823199	2.136614
138.H	-5.090525	-2.517510	2.425008
139.H	3.627815	-3.151817	2.651855
140.H	-7.230912	-1.315051	2.880419

141.C	-0.755076	3.509722	2.498999
142.C	-1.437981	2.265826	2.582161
143.H	0.966624	-7.589644	3.155653
144.C	0.712754	-5.438632	3.229468
145.C	0.253987	-3.027902	3.307574
146.H	-0.221263	5.340160	3.482424
147.H	1.642137	2.169928	3.021912
148.H	-2.450603	-0.139174	3.343972
149.C	-0.743685	4.385256	3.591503
150.H	-0.442995	-0.984562	3.402782
151.C	0.580964	-6.817622	3.834415
152.C	2.264801	0.213584	3.668755
153.C	0.123366	-4.323357	3.830194
154.C	-2.045175	1.926827	3.820201
155.H	-0.467479	-7.059920	4.062484
156.H	-3.834158	0.722941	4.026483
157.H	-1.524416	-2.178721	4.164410
158.C	-0.473928	-1.903944	3.994560
159.C	-2.739855	0.615411	4.076070
160.C	1.881181	1.543944	3.881455
161.H	1.141421	-6.895012	4.779133
162.H	2.894556	-1.628932	4.635623
163.H	-0.473271	-4.455286	4.738535
164.C	-1.382532	4.084670	4.797819
165.C	2.573939	-0.595809	4.778719
166.C	-2.011900	2.842884	4.884468
167.H	-0.034423	-1.670378	4.975193
168.H	-2.487067	0.246939	5.079692
169.H	-1.164542	6.070420	5.641325
170.C	1.806052	2.062154	5.178753
171.H	1.505340	3.100595	5.324139
172.H	-2.498994	2.554892	5.821013
173.C	-1.351574	5.039300	5.969815
174.C	2.485944	-0.081317	6.073204
175.H	-2.299822	5.025413	6.524778
176.C	2.106609	1.251654	6.276138
177.H	-0.556129	4.773018	6.684545
178.H	2.726966	-0.719111	6.925374
179.H	2.051539	1.656849	7.288658

Final energy: –1123.69464435 eV

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