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Merging the Chemistry of Electron-Rich Olefins with Imidazolium Ionic Liquids: Radicals and Hydrogen-Atom Adducts

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Experimental procedures

Sample preparation: Under a dinitrogen atmosphere, 1-ethyl-3-methylimidazolium chloride (9.89 g) was weighed into a round-bottom flask (50 cm^3). To this, aluminium(III) chloride (5.96 g) was added in small increments over the course of ninety minutes, using a Teflon coated micro-spatula. At first, the solids were stirred using a glass stirring rod, eventually forming a paste. At this point, the exothermic nature of the reaction has the potential to char the materials and thus, the aluminium(III) chloride was added particularly slowly and cautiously. Upon further addition, the paste started to liquify, at which point a magnetic stirring bar was used to stir the mixture. Upon completion of the reaction, the resulting product was a slightly viscous, green-yellow ionic liquid. The composition of this basic ionic liquid is 40 mole % aluminium(III) chloride.[1]

EPR measurements: Spectra were collected at room temperature with a Bruker EMXplus EPR spectrometer operating at X-band (~9.5 GHz). Samples were loaded into 4 mm outer-diameter quartz tubes under an inert atmosphere and the tubes were sealed with O-ring needle valves. Sample volumes were ~300 μL.

Muon experiment: The sample was purified by distillation and studied as a neat liquid, prepared under a nitrogen atmosphere and sealed oxygen-free in stainless steel vessels fitted with a thin steel foil window. Spectroscopic experiments were performed at the M20 muon beam line of the TRIUMF cyclotron facility in Vancouver (Canada) using apparatus and measurement procedures reported elsewhere.[2]

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Calculations: Geometry optimisations (tight optimisation criteria) were performed using the Gaussian 09 program (Revision A.02),[3] the B3LYP functional,[4] and the 6-311+g* basis set on all atoms. Frequency calculations at the same level of theory confirmed that the optimised structures were located at a minimum on the potential energy surface. Single point calculations specifically for hyperfine coupling calculations were completed with the B3LYP functional and the EPR-III basis set of Barone[5] on all atoms.

Table S1 Optimised XYZ coordinates (Å) for 6. Tight ub3lyp/6-311+g* all atoms, in vacuum.

Atom Number	Coordinates (Å)		
	X	Y	Z
1	-0.783342	-0.002497	-0.003315
2	0.581977	-0.014287	0.006112
3	-1.588815	-1.107776	0.343146
4	-1.560857	1.120157	-0.359448
5	1.287237	-1.237562	-0.152490
6	1.308816	1.188748	0.180196
7	-1.107390	-2.094572	1.284399
8	-2.497420	-1.637347	-0.662344
9	-1.033819	2.109337	-1.274309
10	-2.488326	1.655054	0.626091
11	1.355158	-1.855700	-1.465175
12	2.445789	-1.487625	0.681803
13	2.454641	1.470955	-0.658085
14	1.310009	1.871145	1.459013
15	-1.966221	-2.584666	1.753978
16	2.303262	-1.041372	1.665781
17	-0.474552	-2.867380	0.827018
18	-2.020176	-2.400334	-1.298108
19	-2.847062	-0.824100	-1.295420
20	-3.363460	-2.099166	-0.179681
21	-1.870021	2.632368	-1.748430
22	-0.448756	1.618160	-2.051604
23	1.258294	2.958217	1.319990
24	-3.333903	2.134454	0.124634
25	-2.017507	2.404351	1.282424
26	-2.867588	0.841251	1.241036
27	1.420897	-2.945120	-1.370181
28	2.228058	-1.523859	-2.054221
29	0.454580	-1.619398	-2.028132
30	2.579541	-2.565817	0.818955
31	-0.522877	-1.605685	2.063631
32	3.384738	-1.094123	0.261513
33	2.526624	2.547758	-0.850717
34	2.348953	0.968590	-1.618795
35	3.410516	1.156790	-0.210368
36	2.215535	1.657929	2.052757
37	0.441958	1.563931	2.038413
38	-0.389151	2.855484	-0.789444

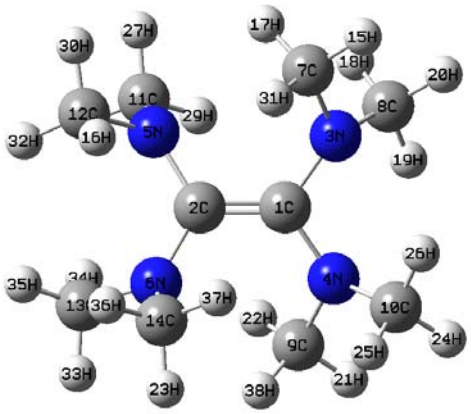

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Table S2 Optimised XYZ coordinates (Å) for 7. Tight ub3lyp/6-311+g* all atoms, in vacuum.

Atom number	Coordinates (Å)		
	X	Y	Z
1	-0.634139	-0.007957	0.093934
2	-1.004304	-0.793342	-1.001892
3	-1.611450	0.757073	0.784935
4	-1.849069	0.514862	2.200876
5	-2.268505	1.411094	2.669121
6	-2.552567	-0.317996	2.374170
7	-0.916936	0.273770	2.709943
8	-2.154837	-1.673618	-0.914541
9	-3.052812	-1.261180	-1.399652
10	-1.932633	-2.630998	-1.404288
11	-2.390772	-1.878743	0.129777
12	-0.580288	-0.495555	-2.363189
13	-0.401289	-1.425462	-2.915279
14	-1.343695	0.075825	-2.919395
15	0.343595	0.077955	-2.347653
16	-2.794987	1.209475	0.075678
17	-3.630275	0.492633	0.113382
18	-3.150911	2.146821	0.518098
19	-2.558068	1.399936	-0.971127
20	0.822289	0.224801	0.449272
21	0.808465	0.734646	1.430531
22	1.549217	1.110741	-0.503597
23	1.632120	-0.984968	0.666740
24	1.237166	-1.743838	1.836937
25	0.255526	-2.239784	1.735299
26	1.983433	-2.518886	2.033596
27	1.198692	-1.093304	2.715144
28	2.903644	1.414635	-0.043718
29	2.906481	1.970248	0.912979
30	3.473172	0.499949	0.100732
31	3.407164	2.031482	-0.792602
32	0.830725	2.353833	-0.757759
33	1.384060	2.943844	-1.492772
34	-0.161496	2.156255	-1.161491
35	0.706453	2.970516	0.150653
36	1.887829	-1.838441	-0.485249
37	2.725542	-2.504184	-0.251660
38	1.027886	-2.462702	-0.772312
39	2.170416	-1.227433	-1.341937

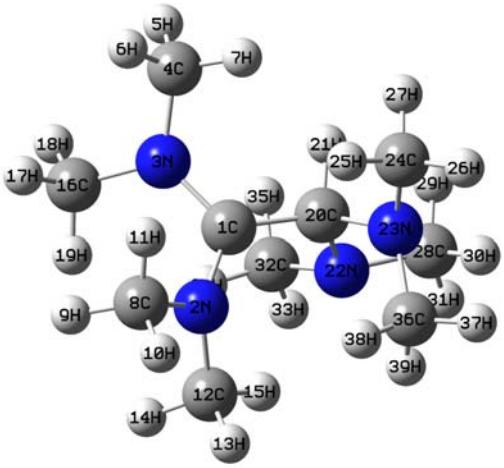

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Table S3 Optimised XYZ coordinates (Å) for 8. Tight ub3lyp/6-311+g* all atoms, in vacuum.

Atom number	Coordinates (Å)		
	X	Y	Z
1	1.518863	-0.115591	0.038428
2	1.186499	1.223254	0.088602
3	-0.150791	1.311245	-0.133555
4	-0.619220	0.026492	-0.320676
5	-2.031348	-0.356713	-0.559328
6	-2.882055	-0.259728	0.699903
7	2.866410	-0.671149	0.223505
8	0.409360	-0.816370	-0.209143
9	1.920312	1.988750	0.271036
10	-0.796901	2.170131	-0.181262
11	-2.015697	-1.372547	-0.952174
12	-2.404701	0.295015	-1.348819
13	-3.903318	-0.558241	0.461084
14	-2.914677	0.759011	1.087625
15	-2.510176	-0.920628	1.483761
16	2.825230	-1.749223	0.091681
17	3.219483	-0.441837	1.227174
18	3.539414	-0.242766	-0.516641
19	0.355080	-1.887198	-0.307639

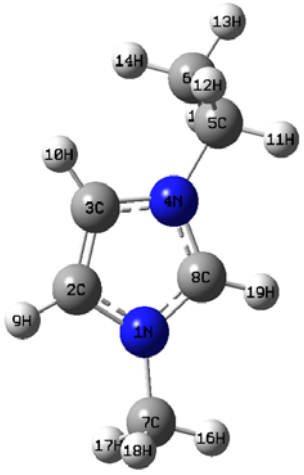

Table S4 Optimised XYZ coordinates (Å) for 9. Tight ub3lyp/6-311+g* all atoms, in vacuum.

Atom number	Coordinates (Å)		
	X	Y	Z
1	0.638091	-0.144087	-0.121761
2	-0.525032	-0.958047	-0.091534
3	-1.606274	-0.051008	-0.219755
4	-1.114706	1.229087	0.013900
5	0.230587	1.176353	0.073644
6	-1.767690	2.084421	0.061519
7	0.934191	1.983923	0.174462
8	-2.956108	-0.452233	0.112317
9	1.906115	-0.672392	0.364349
10	3.114239	0.079813	-0.180889
11	-3.652424	0.333577	-0.182586
12	-3.074271	-0.654898	1.185241
13	-3.213047	-1.358747	-0.437909
14	1.951116	-1.716164	0.048217
15	1.918914	-0.675675	1.463941
16	4.033806	-0.393606	0.168993
17	3.134709	1.117977	0.155801
18	3.116389	0.075022	-1.272300
19	-0.534976	-1.845659	-0.725489

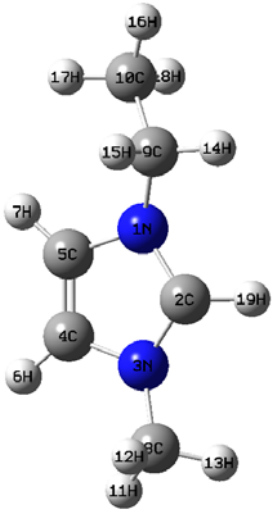

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Table S5 Optimised XYZ coordinates (Å) for 10. Tight ub3lyp/6-311+g* all atoms, in vacuum.

Atom number	Coordinates (Å)		
	X	Y	Z
1	0.747961	-1.297056	-0.982825
2	1.464660	-0.608010	-1.950150
3	2.026412	0.485147	-1.388686
4	1.683697	0.527736	-0.046554
5	-1.380161	0.754131	-0.430142
6	-0.764100	0.071508	0.658013
7	-1.668807	-0.996164	0.939109
8	-2.612135	-1.064515	-0.065179
9	-2.442013	0.001304	-0.886464
10	-1.194003	2.177311	-0.724655
11	-2.061828	3.094307	0.136666
12	-1.609426	-1.815554	2.132874
13	2.430486	1.249806	0.983160
14	3.665351	0.504126	1.489324
15	0.539161	-2.737894	-1.020572
16	0.788294	-0.549663	0.231288
17	1.498573	-0.946035	-2.971852
18	2.622142	1.258279	-1.844002
19	-0.548183	0.704738	1.524527
20	-3.331643	-1.863605	-0.117956
21	-3.004411	0.284955	-1.759613
22	-1.421463	2.317012	-1.782331
23	-0.137623	2.408822	-0.595320
24	-1.881968	4.135896	-0.134870
25	-1.834453	2.982765	1.198753
26	-3.122222	2.884279	-0.009708
27	-2.493880	-2.448185	2.172006
28	-1.596378	-1.189152	3.028156
29	-0.725932	-2.460904	2.145459
30	1.749306	1.464132	1.810175
31	2.716633	2.213635	0.558627
32	4.176520	1.103142	2.244734
33	4.366400	0.312357	0.675972
34	3.399943	-0.451402	1.945854
35	-0.360311	-3.006224	-0.470948
36	1.394015	-3.278997	-0.600509
37	0.406430	-3.047296	-2.055745
38	1.064520	-1.145966	1.107748

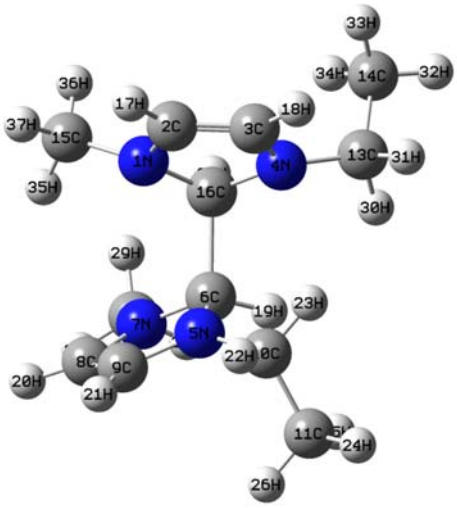

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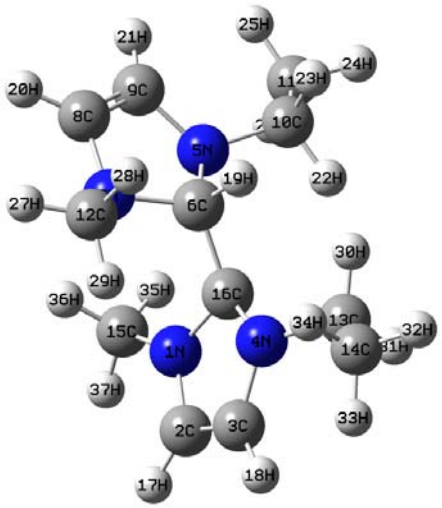
Table S6 Optimised XYZ coordinates (Å) for 11. Tight ub3lyp/6-311+g* all atoms, in vacuum.

Atom number	Coordinates (Å)		
	X	Y	Z
1	0.724235	-1.027921	-1.403335
2	2.063772	-1.253934	-1.624447
3	2.786560	-0.414521	-0.855023
4	1.909321	0.348214	-0.070033
5	-1.864950	0.365964	-0.054926
6	-0.533185	0.040665	0.506723
7	-0.790104	-1.255203	1.189074
8	-2.169312	-1.251027	1.486510
9	-2.792512	-0.311291	0.767492
10	-2.070845	1.779694	-0.346042
11	-3.319529	2.038277	-1.180766
12	0.147219	-1.591277	2.244240
13	2.266663	1.712524	0.320135
14	3.473146	1.765989	1.250371
15	-0.361882	-1.748503	-2.029513
16	0.573868	0.050277	-0.503173
17	2.401012	-2.010841	-2.312705
18	3.854456	-0.318960	-0.774725
19	-0.273237	0.797378	1.285912
20	-2.601901	-2.023009	2.103583
21	-3.851841	-0.145184	0.665909
22	-1.189112	2.111851	-0.898538
23	-2.110376	2.367585	0.587570
24	-3.404372	3.103515	-1.406216
25	-4.231261	1.741342	-0.658527
26	-3.274149	1.489382	-2.123130
27	-0.142737	-2.539379	2.699874
28	0.184292	-0.821374	3.033265
29	1.147846	-1.704125	1.827760
30	1.400740	2.140412	0.824530
31	2.444948	2.323582	-0.576850
32	3.666875	2.798918	1.546889
33	4.377860	1.389767	0.769661
34	3.295475	1.175814	2.151074
35	-1.131696	-1.050158	-2.358897
36	-0.821746	-2.457109	-1.336208
37	0.025636	-2.288033	-2.894735



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