A metallacyclic alkyl-amido carbene complex (MCAAC)

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Fig. S1. Calculated structure and HOMO of $[3q]^+$; calculated structure and spin density of $[3q]^{2+}$.

Fig. S2. Molecular core structure of **2**, without any bond lengths and angles due to the low quality of the refinement.

Fig. S3. ¹H, ¹³C-gHMQC NMR correlation spectrum of **3**.

Fig. S4. Detail of the ¹H, ¹⁵N-gHMQC NMR correlation spectrum of **3**.

Fig. S5. Detail of the ¹H, ¹H-gNOESY NMR correlation spectrum of **3**.

Coordinates of the calculated structures.



Fig. S1. Calculated structure of $[3q]^+$ (a) and HOMO of $[3q]^+$ (b); calculated structure of $[3q]^{2+}$ (c) and spin density of $[3q]^{2+}$ (d).



Fig. S2. Preliminary molecular structure of 2 (cationic part; anisotropic displacement parameters at the 30% probability level). The counter ion has been ommitted for clarity. Due to the low quality of the crystal refinement, no bond lengths and angles are discussed. Lattice constants: a = 9.763(2), b = 19,857(4), c = 22.899(5) Å, $\beta = 97.37(3)^{\circ}$.



Fig. S3. ¹H,¹³C-gHMQC NMR correlation spectrum of **3** (a); details of the ¹H,¹H-gCOSY NMR correlation spectrum of **3** (b and c).



Fig. S4. Detail of the ¹H, ¹⁵N-gHMBC NMR correlation spectrum of **3**.



Fig. S5. Detail of the ¹H, ¹H-gNOESY NMR correlation spectrum of **3**.

Coordinates of $[3q]^+$

Н	-2	•	31	13	1	88 38		1	• : `	56	56 24	5	3	7	a		4	י ז	3	22	27	8	7	7
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С	-1	•	59	97	9	71		1	•	78	36	4	7	3		-	2	•	2	4 !	55	2	1	
Η	-1	•	18	32	6	60		2	•	78	30	5	1	4		- 1	2	•	1	42	29)3	8	
С	-2		95	54	9	24		- (3	. 4	11	4	6	4	0		-	1	•	6!	51	0	8	8
Η	1.	5	64	17	1	6	1	•	25	50	0 (8	1		-	1	•	7	7	2	95	6		
Η	1.	3	22	22	4	1	-	1	• -	12	23	1	6	4		-	1	•	9	1(03	80	2	
Н	-0	•	82	26	3	98			4	. 1	. 3	6	4	3	5		-	1		6	30	0	0	6
Ν	-2		18	38	3	64		- (C	. 2	28	9	5	6	8		-	1		5	87	8	4	1
С	2.	3	33	38	0	5	_	0	. 8	31	4	7	0	8		-	1		6	1,	46	59	3	
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Н	-4		96	56	0	82		-2	2	. 9	95	6	1	7	9		_	0		7:	34	7	5	5
Н	3.	3	6()5	1	2	2		42	24	16	1	0		_	0		7	1	1:	37	0		
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Н	5.	4	85	54	2	9	1		4 9	94	11	8	9		_	0		4	3	1:	17	0		
Ν	-1		63	39	1	26	,	0	. 8	3 9	98	3	6	5		_	1		1	9	92	26	9	
С	3.	3	62	23	5	6	1		3:	37	73	6	8	-	_	0		6	2	1:	13	34	-	
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С	2.	8	54	42	4	8	_	1		73	38	4	9	6		_	0		4	91	05	54	9	
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С	-1		92	26	4	38		-:	3	. 9	97	5	0	1	8		0		3	4	64	6	0	
С	-3		26	59	3	78		-:	3	. 5	58	4	3	4	1		0		6	21	83	31	7	
Н	-2		35	53	1	46	;	3	. (61	. 5	6	4	9		0		0	5	6!	55	;9		
Н	-0		54	45	3	05)	5	. (62	24	4	0	4		0	•	5	8	31	06	54		
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Н	5.	5	23	35	0	3	_	0	. 8	36	52	4	7	5		0		9	4	9	63	88		
С	-1		29	94	6	05)	3		56	59	5	2	1		0	•	2	8	7	16	54		
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С	0.	0	69	90	4	8	0) (14	18	3	6		0		3	8	1	5	60)		
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Н	-1	•	19	99	3	65)		4	.3	31	1	6	8	5		1		0	81	03	31	9	
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Н	5.	3	20	65	8	1	0		71	10)5	3	9		1		7	2	8	1'	73	8		
Ir	1	•	86	65	1	78	;	0	. 8	38	32	8	1	5		0		9	7	0	01	.7		
С	2.	5	99	91	4	6	-	1	• 2	20)5	3	3	6		0		9	2	0	18	31		
Ν	-2		82	26	0	66)	- 1	С	. 4	14	2	6	5	0		1	•	1	0	07	5	4	
Ν	-2		18	34	5	69)	0	•	76	51	6	4	5		1	•	1	4	6	15	6		
С	3.	5	43	34	2	8	_	0	• 4	43	30	0	8	8		1	•	6	1	3	13	81		
Cl	3	•	34	10	8	57		2	• 4	48	86	4	9	5		2	•	1	2	4	16	7		
Η	1.	9	14	18	5	1	-	1	•	77	1	7	8	4		1	•	5	5	82	29	8		
С	-3	•	68	39	3	94		- (С.	. 4	13	0	1	5	6		2	•	1	2	94	5	7	
Η	-4	•	33	38	3	81		- :	1.	. 2	28	1	2	4	9		2	•	2	98	80	1	0	

С	-2.	602	650	1.50	249	95 2	2.221	457
Η	3.4	823	59 -	0.42	463	37 3	2.703	884
Η	-2.	163	134	2.45	983	32 2	2.467	354
С	-3.	581	340	0.76	575	52 2	2.857	212
Cl	0.	824	660	0.57	176	51 3	3.103	230
Н	-4.	135	081	1.05	218	36	3.743	396

Coordinates of $[3q]^{2+}$

Н -3.027677 0.236205 -4.295536 Н -2.741436 -2.249335 -3.159450 C -2.687232 -0.005624 -3.295014 C -2.545283 -1.275444 -2.725530 Н -1.880328 -4.481914 -2.256805 Н 3.100191 0.069982 -2.657635 C -2.308008 0.889643 -2.308908 н -2.265623 1.971905 -2.319947 C -1.583098 -4.421179 -1.213147 H 1.046095 1.658647 -1.990812 H 1.639286 -0.660734 -2.024430 H 0.631137 -4.075454 -1.352601 N -2.099866 -1.177781 -1.456683 C 2.478954 -0.007755 -1.748756 H 4.640499 1.684646 -1.352968 H -3.514049 -4.813769 -0.123005 H 2.303322 3.418249 -0.983845 C -0.255435 -4.190523 -0.735621 C 1.931343 1.363956 -1.418972 C -2.445759 -4.614339 -0.085698 Н 4.617106 3.305716 -0.677326 N -1.973210 0.159783 -1.201885 C 2.689322 2.405768 -0.853578 C 4.182558 2.304445 -0.568139 н 4.357323 -0.424479 -0.715085 C 3.287581 -0.643993 -0.596040 Н 3.213048 -1.739841 -0.657083 Ru -1.509245 -2.541802 -0.024389 C -0.304870 -4.224690 0.710895 C -1.652233 -4.481462 1.097804 н -3.505641 2.609910 -0.127159 H -2.471620 5.134087 0.206784 C -1.438012 0.604832 0.112557 Н 5.474311 1.176292 0.797722 C -2.486391 2.933272 0.057873 C -1.944451 4.186753 0.229767 N 0.072768 -1.215437 0.183216 N -1.450594 2.031528 0.161773 C -0.562902 3.988707 0.450468 C 4.539791 1.763747 0.837228 Н 0.224838 4.703196 0.668598 C 0.026755 0.069928 0.280114 N -0.272080 2.688184 0.408635 H 1.003032 -1.619700 0.297884 н 0.535073 -4.116490 1.392240 Н -2.007592 -4.577212 2.120419 Н 4.728937 2.602797 1.514135 Ir 1.413289 1.514899 0.773636

C 2.860468 -0.182630 0.798938 N -2.439542 -1.288114 1.313519 N -2.289581 0.066074 1.195754 C 3.473494 0.894514 1.455444 Cl 2.218677 3.523033 1.875746 H 2.423841 -0.929910 1.469028 C -3.123072 -1.485170 2.462545 H -3.394686 -2.489430 2.767604 C -2.817663 0.703025 2.281528 H 3.407177 0.919499 2.545801 H -2.760713 1.777663 2.403383 C -3.380766 -0.267446 3.095403 Cl 0.523738 0.945656 2.929553 H -3.905300 -0.104889 4.030054