Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Emergent property of high hardness for the C-rich ruthenium carbides: partial covalent Ru-Ru bonds

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Figure S1. The relative formation enthalpies (the left) and the relative energy-volume curves (the right) of *R*-3*m*-RuC, *I*4*mm*-RuC, and *P*-3*m*1-RuC compared to Exp-RuC.

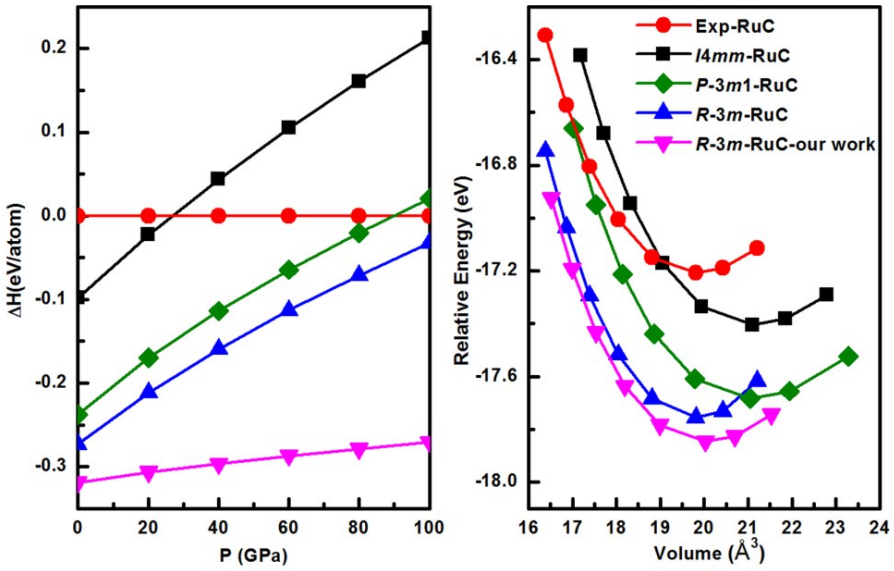


Figure S2. The simulated power X-ray diffraction and the diffraction data are obtained from powder diffraction for (a) *R*-3*m*-RuC in Zhang's work, (b)*R*-3*m*-RuC in our work.

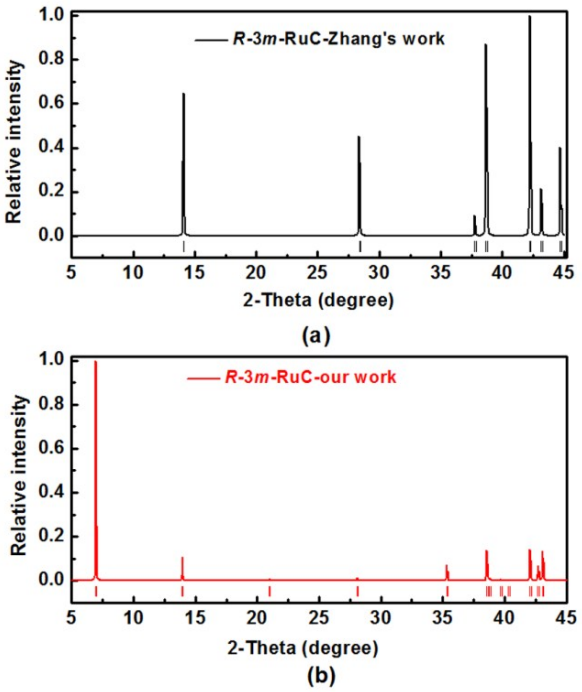


Figure S3. The relative enthalpies of *P*2/*m*-Ru_2C_3 compared to *P*-4*c*2-Ru_2C_3 (a), *Cmmm*-RuC_2, *P*-3*m*1-RuC_2 compared to *Pnnm*-RuC_2 (b), *P*-3*m*1-RuC_4, and *R*-3*m*-RuC_4 compared to *Cmmm*-RuC_4 (c).

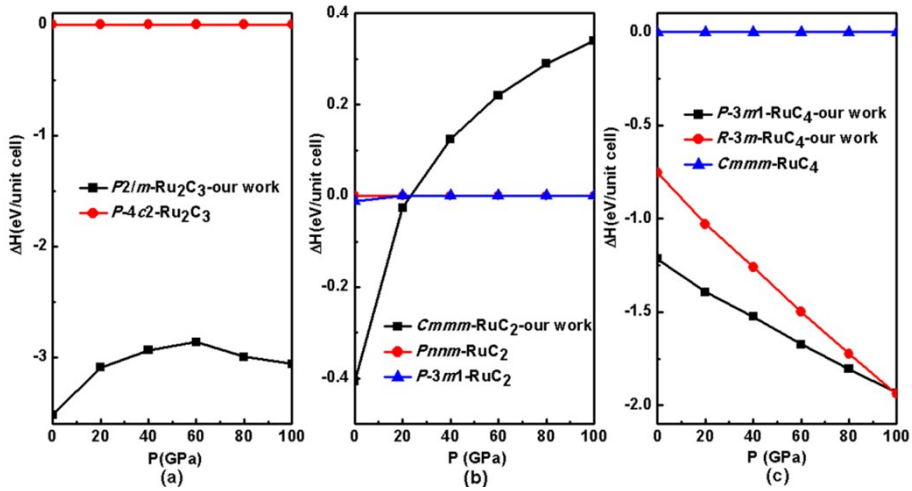
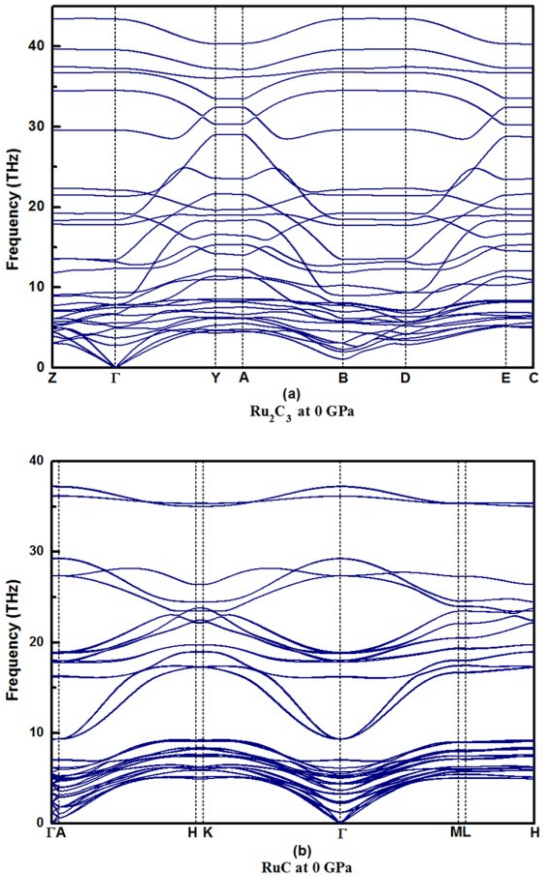
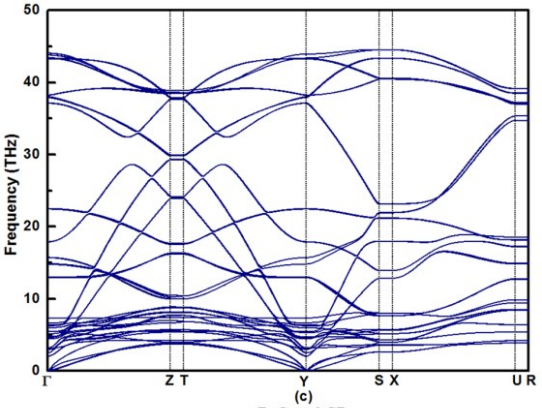
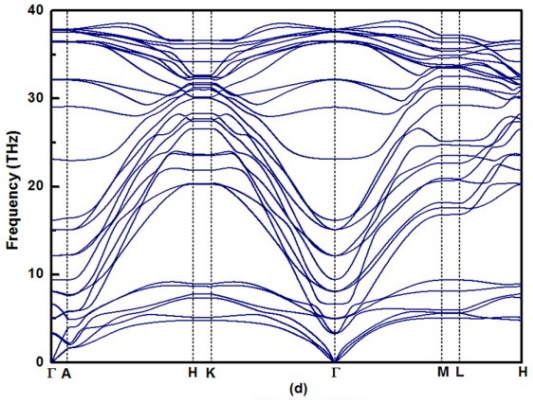


Figure S4. Phonon dispersions for the stable C-rich ruthenium carbides at different pressures.

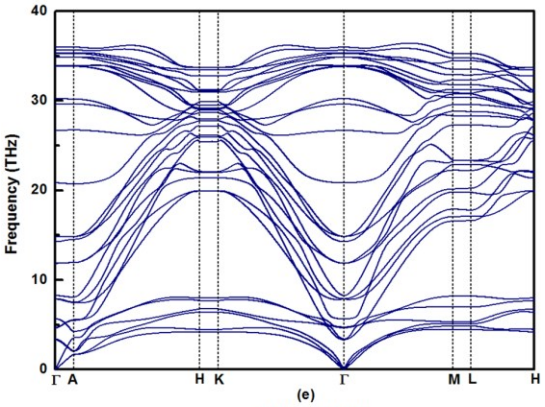




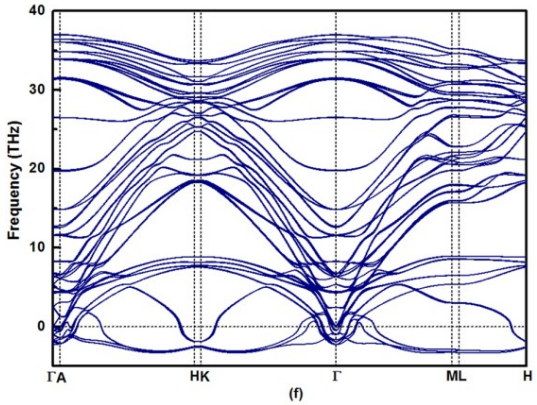
(c)
RuC_2 at 0 GPa



(d)
P-RuC_4 at 30 GPa



(e)
P-RuC_4 at 0 GPa



(f)
R-RuC_4 at 0 GPa

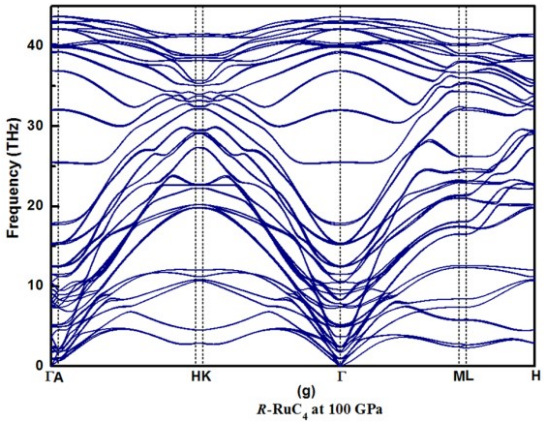


Table S1. Detailed structure information of Ru_2C_3 (SG: *P*2/*m*) at 0 GPa.

a, b, c [Å]	9.76260	2.63860	4.21230	Volume (Å^3)
α, β, γ [˚]	90.0000	92.7541	90.0000	108.381816
Ru (2n)	0.82396	0.50000	0.74658	
Ru (2m)	0.08025	0.00000	0.75811	
C (2n)	0.23818	0.50000	0.77444	
C (2n)	0.63563	0.50000	0.39296	
C (2m)	0.56645	0.00000	0.44472	

Table S2. Detailed structure information of RuC (SG: *R*-3*m*) at 0 GPa.

a, b, c [Å]	2.69920	2.69920	38.09560	Volume (Å^3)
α, β, γ [˚]	90.0000	90.0000	120.0000	240.367394
Ru (6c)	0.33333	0.66667	0.36215	
Ru (6c)	0.33333	0.66667	0.24626	
C (6c)	0.00000	0.00000	0.21250	
C (6c)	0.66667	0.33333	0.15971	

Table S3. Detailed structure information of RuC_2 (SG: *Cmmm*) at 0 GPa.

a, b, c [Å]	23.50390	4.29630	2.55480	Volume (Å^3)
α, β, γ [˚]	90.0000	90.0000	90.0000	257.983213
Ru (4h)	0.81889	0.50000	0.50000	
Ru (4g)	0.77856	0.00000	0.00000	
C (8q)	0.91194	0.33034	0.50000	
C (8p)	0.91524	0.16463	0.00000	

Table S4. Detailed structure information of RuC_4 (SG: *P*-3*m*1) at 0 GPa.

a, b, c [Å]	2.56020	2.56020	13.18280	Volume (Å^3)
α, β, γ [˚]	90.0000	90.0000	120.0000	74.831781
Ru (2d)	-1.33333	-0.66667	0.08427	
C (2d)	0.66667	0.33333	0.71713	
C (2d)	0.66667	0.33333	0.59726	
C (2d)	1.33333	0.66667	0.75345	
C (2c)	-1.00000	-1.00000	0.44080	

Table S5. Detailed structure information of RuC_4 (SG: *R*-3*m*) at 100 GPa.

a, b, c [Å]	2.43340	2.43340	35.61660	Volume (Å^3)
α, β, γ [°]	90.0000	90.0000	120.0000	182.645959
Ru (6c)	1.66667	0.33333	0.02830	
C (6c)	0.00000	1.00000	0.24192	
C (6c)	0.00000	1.00000	0.20053	
C (6c)	-0.33333	1.33333	0.25560	
C (6c)	1.33333	0.66667	0.14608	

Table S6. Calculated Elastic Constants C_{ij}s (GPa) of known structures of RuC at 0 GPa.

Phase	Space group		P	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}
RuC	*R*-3*m*		0	514		587	135		179	155	169
	R-3*m*	Ref10	0	539		581	176		194	152	178
	R-3*m*	Ref20	0	504		613	161		163	178	189
	*I*4/*mm*		0	564		459	57		82	217	201
	*I*4/*mm*	Ref11	0	516		427	63		75	212	182
	F-43*m*		0	347			62			222	
	F-43*m*	Ref10	0	345			66			216	
	P-6*m*2		0	452		873	97			349	173
	P-6*m*2	Ref11	0	396		700	76			307	199

Table S7. Calculated Bulk Moduli B (GPa), Shear Moduli G (GPa), B/G Ratio, Possion's ratio ν and Vickers Hardness H_v (GPa) of known structures of RuC at 0 GPa.

Phase	Space group		P	B	G	B/G	ν	H_v
RuC	*R*-3*m*		0	288	160	1.80	0.27	16.6
	R-3*m*	Ref10	0	296	186	1.59	0.24	27.4-28.0
	R-3*m*	Ref20	0	302	167	1.80		17.0
	*I*4/*mm*		0	312	94	3.33	0.36	4.0
	*I*4/*mm*	Ref11	0	286	85	3.36		
	F-43*m*		0	264	62	4.29	0.39	1.1
	F-43*m*	Ref10	0	259	64	3.95		42.8
	P-6*m*2		0	348	100	3.47	0.37	3.9
	P-6*m*2	Ref11	0	316	66	4.79		

Table S8. Calculated Bulk Moduli B (GPa), Shear Moduli G (GPa), B/G Ratio, Possion's ratio ν and Vickers Hardness H_v (GPa) of transition metal carbides Os_2C_3, TiC, HfC, TaC, OsC, WC, OsC_4 at 0 GPa.

Phase	Space group	B	G(GPa)	B/G	v	H_v (GPa)
Os_2C_3	*P*-4*c*2	327	138	2.36	0.32	10.0
		332[27]	152[27]	2.18[27]	0.30[27]	19.8[27]
TiC	*Fm*-3*m*	252	178	1.41	0.21	24.6
HfC	*Fm*-3*m*	252	176	1.43	0.22	24.1
TaC	*Fm*-3*m*	338	198	1.71	0.26	20.6
WC	*P*-6*m*2	398	276	1.44	0.22	31.9
OsC_4	*Cmmm*	380	293	1.30	0.19	37.9
		379[3]	280[3]			37.0[3]

Table S9. Bader charge analysis using supercell calculations 2×2×1 of Ru_2C_3,RuC and *P*-RuC_4 and *R*-RuC_4 at different pressures.

Ru_2C_3 (P = 0 GPa)					
Atom (Number)	**Charge value**	**δ(e)**	**Atom (Number)**	**Charge value**	**δ(e)**
Ru (16)	7.74	+0.26	C (16)	4.04	-0.04
Ru (16)	7.73	+0.27	C (8)	4.05	-0.05
Ru (16)	7.73	+0.27	C (16)	4.48	-0.48
			C (8)	3.98	+0.02
RuC (P = 0 GPa)					
Atom (Number)	**Charge value**	**δ(e)**	**Atom (Number)**	**Charge value**	**δ(e)**
Ru (8)	7.62	+0.38	C (8)	4.02	-0.02
Ru (16)	7.63	+0.37	C (8)	4.32	-0.32
Ru (14)	8.04	-0.04	C (8)	4.33	-0.33
Ru (3)	8.03	-0.03	C (8)	4.34	-0.34
Ru (5)	8.05	-0.05	C (4)	3.98	+0.02
Ru (1)	8.06	-0.06	C (8)	3.99	+0.01

***P*-RuC_4 (P = 0 GPa)**					
Atom (Number)	**Charge value**	**δ(e)**	**Atom (Number)**	**Charge value**	**δ(e)**
Ru (1)	7.84	+0.14	C (24)	4.05	-0.05
Ru (8)	7.85	+0.15	C (16)	4.13	-0.13
Ru (6)	7.86	+0.16	C (8)	3.94	+0.06
Ru (1)	7.87	+0.17	C (16)	3.97	+0.03
***R*-RuC_4 (P = 100 GPa)**					
Atom (Number)	**Charge value**	**δ(e)**	**Atom (Number)**	**Charge value**	**δ(e)**
Ru (2)	7.71	+0.29	C (4)	4.00	0.00
Ru (5)	7.72	+0.28	C (8)	4.01	-0.01
Ru (1)	7.73	+0.27	C (16)	4.03	-0.03
Ru (4)	7.74	+0.26	C (8)	4.04	-0.04
Ru (4)	7.75	+0.25	C (16)	4.05	-0.05
Ru (4)	7.77	+0.23	C (8)	4.06	-0.06
Ru (2)	7.78	+0.22	C (8)	4.21	-0.21
Ru (2)	7.79	+0.21	C (8)	4.22	-0.22
			C (8)	4.23	-0.23

Figure S5. Plots of the Crystal orbital Hamilton population (COHP) for (a) Ru_2C_3, (b) RuC.

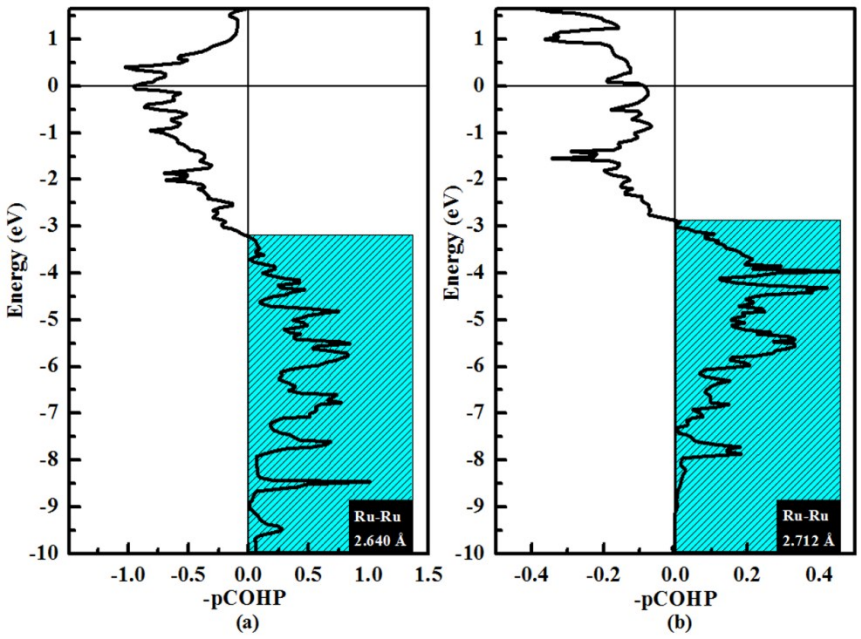


Figure S6. The 2D electron localization function (ELF) slice of (a) the graphene-like C_6 ring and (b) the (010) planes in the Ru_2C_3 at 0 GPa (c) the (110) planes in the RuC at 0 GPa. (d) the (110) planes in the *P*-RuC_4 at 0 GPa. (e) the (110) planes in the *R*-RuC_4 at 100 GPa. The isosurface of the electron localization function with an isovalue of 0.8. The green balls represent C atoms, and orange balls represent Ru atoms.