Multiple bonding versus cage formation in organophosphorus compounds: the gas-phase structures of tricyclo-$P_3(CBu^t)_2Cl$ and $P{\equiv}C–Bu^t$ determined by electron diffraction and computational methods

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Electronic Supplementary Information

Table S1 Nozzle-to-film distances / mm, weighting functions / nm^{-1}, scale factors, correlation parameters and electron wavelengths / pm used in the electron diffraction studies of tricyclo-$P_3C_2(Bu^t)_2Cl$ and $P{\equiv}C–Bu^t$.

	Nozzle-to-film distance[a]	Δs	s_{min}	sw_1	sw_2	s_{max}	Scale factor[b]	Correlation parameter	Electron wavelength
$P_3C_2(Bu^t)_2Cl$	249.8	1	20	40	129	150	0.632(6)	0.489	6.18
	89.4	2	70	90	276	320	0.678(13)	0.191	6.18
$P{\equiv}C–Bu^t$	290.9	1	20	40	112	130	0.760(1)	0.492	6.13
	130.4	2	80	100	258	300	0.774(8)	0.284	6.13

[a] Determined by reference to the scattering pattern of benzene. [b] Values in parentheses are the estimated standard deviations.

Table S2 Interatomic distances (r_a / pm), refined and calculated amplitudes of vibration (u / pm) and distance corrections (k_{h1} / pm) for the SARACEN-restrained GED structure of tricyclo-$P_3C_2(Bu^t)_2Cl$.[a]

	Atom pair	r_a	u(exp.)[b]	k_{h1}	u(calc.)
u_{27}	C(10)–H(18)	110.5(2)	7.2(2)	0.4	7.5
u_{28}	C(10)–H(19)	110.5(2)	7.2(tied to u_{27})	0.4	7.5
u_{26}	C(9)–H(15)	110.5(2)	7.2(tied to u_{27})	0.4	7.5
u_{29}	C(8)–H(13)	110.5(2)	7.2(tied to u_{27})	0.4	7.5
u_{24}	C(10)–H(17)	110.5(2)	7.2(tied to u_{27})	0.4	7.5
u_{23}	C(9)–H(16)	110.5(2)	7.2(tied to u_{27})	0.4	7.5
u_{22}	C(8)–H(11)	110.5(2)	7.2(tied to u_{27})	0.4	7.5
u_{25}	C(9)–H(14)	110.5(2)	7.2(tied to u_{27})	0.4	7.5
u_{21}	C(8)–H(12)	110.5(2)	7.2(tied to u_{27})	0.4	7.4
u_{30}	C(3)–C(7)	153.4(3)	4.1(2)	0.1	5.0
u_{31}	C(7)–C(10)	154.4(1)	4.1(tied to u_{30})	0.1	5.1
u_{32}	C(7)–C(9)	154.4(1)	4.1(tied to u_{30})	0.2	5.1
u_{33}	C(7)–C(8)	154.4(1)	4.1(tied to u_{30})	0.2	5.1
u_{36}	H(11)···H(12)	181.2(7)	11.9(fixed)	0.0	11.9
u_{39}	H(14)···H(16)	181.2(7)	11.9(fixed)	0.0	11.9
u_{34}	H(17)···H(19)	181.3(7)	11.9(fixed)	0.0	11.9
u_{35}	H(17)···H(18)	181.3(7)	11.9(fixed)	0.0	11.9
u_{42}	H(18)···H(19)	181.3(7)	11.9(fixed)	0.0	11.9
u_{40}	H(14)···H(15)	181.3(7)	11.9(fixed)	0.0	11.9
u_{37}	H(15)···H(16)	181.3(7)	11.9(fixed)	0.0	11.9
u_{41}	H(11)···H(13)	181.3(7)	11.9(fixed)	0.0	11.9
u_{38}	H(12)···H(13)	181.3(7)	11.9(fixed)	0.0	11.9
u_{43}	P(1)–C(3)	183.1(3)	4.0(2)	0.1	5.1
u_{44}	C(3)–P(4)	187.0(3)	4.3(tied to u_{43})	0.1	5.5
u_{45}	C(3)–P(5)	190.8(3)	4.6(tied to u_{43})	0.2	5.8
u_1	P(4)–P(5)	214.5(13)	5.4(tied to u_2)	0.0	4.8
u_{51}	C(7)···H(16)	215.1(8)	11.8(tied to u_2)	–0.1	10.5
u_{53}	C(7)···H(19)	215.1(8)	11.8(tied to u_2)	–0.1	10.5
u_{46}	C(7)···H(17)	215.1(8)	11.8(tied to u_2)	–0.1	10.5
u_{54}	C(7)···H(18)	215.1(8)	11.8(tied to u_2)	–0.1	10.5
u_{49}	C(7)···H(11)	215.1(8)	11.8(tied to u_2)	–0.1	10.5
u_{50}	C(7)···H(14)	215.1(8)	11.8(tied to u_2)	–0.1	10.5
u_{52}	C(7)···H(12)	215.1(8)	11.8(tied to u_2)	–0.1	10.4
u_{48}	C(7)···H(15)	215.2(8)	11.8(tied to u_2)	–0.1	10.5
u_{47}	C(7)···H(13)	215.2(8)	11.8(tied to u_2)	–0.1	10.5
u_2	P(1)–Cl(6)	216.6(15)	6.7(2)	0.2	5.9
u_3	C(2)···C(3)	226.6(5)	6.1(tied to u_2)	0.1	5.4
u_{66}	H(11)···H(19)	244.1(38)	25.1(fixed)	2.9	25.1
u_{65}	H(12)···H(16)	245.1(37)	24.9(fixed)	3.1	24.9
u_{55}	H(13)···H(17)	248.4(28)	23.7(fixed)	3.3	23.7
u_{60}	C(3)···C(8)	249.5(4)	6.9(tied to u_4)	0.0	7.3
u_{58}	C(3)···C(9)	249.5(4)	6.8(tied to u_4)	0.0	7.2

u_{56}	C(8)···C(10)	250.8(14)	7.0(tied to u_4)	0.0	7.4
u_{62}	C(3)···C(10)	251.6(6)	6.8(tied to u_4)	0.0	7.1
u_{63}	H(13)···H(15)	251.6(28)	24.4(fixed)	3.2	24.4
u_{59}	C(8)···C(9)	252.0(14)	7.1(tied to u_4)	0.0	7.4
u_{61}	H(15)···H(17)	252.4(38)	24.2(fixed)	3.3	24.2
u_{64}	H(14)···H(18)	254.6(57)	25.0(fixed)	3.1	25.0
u_{57}	C(9)···C(10)	254.9(21)	7.1(tied to u_4)	0.0	7.4
u_4	P(1)···P(5)	262.6(5)	6.4(2)	–0.1	6.8
u_{77}	C(8)···H(19)	269.8(24)	16.5(tied to u_4)	0.2	17.3
u_{82}	C(3)···H(12)	269.9(8)	15.6(tied to u_4)	0.2	16.3
u_{81}	C(3)···H(14)	269.9(8)	16.0(tied to u_4)	0.3	16.8
u_{76}	C(3)···H(11)	269.9(8)	15.9(tied to u_4)	0.3	16.7
u_{78}	C(3)···H(16)	269.9(8)	15.8(tied to u_4)	0.3	16.6
u_{79}	C(10)···H(11)	270.5(24)	16.5(tied to u_4)	0.2	17.3
u_{80}	C(8)···H(16)	271.1(23)	16.5(tied to u_4)	0.2	17.3
u_{73}	C(9)···H(12)	271.1(23)	16.3(tied to u_4)	0.3	17.1
u_{67}	C(10)···H(13)	271.7(17)	15.8(tied to u_4)	0.4	16.6
u_{68}	C(8)···H(17)	272.3(17)	15.9(tied to u_4)	0.3	16.7
u_{83}	C(3)···H(19)	272.5(10)	15.5(tied to u_4)	0.3	16.3
u_{84}	C(3)···H(18)	272.6(10)	15.4(tied to u_4)	0.3	16.1
u_{72}	C(9)···H(13)	274.0(17)	16.0(tied to u_4)	0.3	16.8
u_{71}	C(8)···H(15)	274.1(17)	16.2(tied to u_4)	0.4	17.0
u_{70}	C(10)···H(15)	275.4(26)	16.2(tied to u_4)	0.4	17.0
u_{69}	C(9)···H(17)	276.0(26)	16.0(tied to u_4)	0.3	16.8
u_{74}	C(9)···H(18)	276.4(36)	16.4(tied to u_4)	0.2	17.3
u_{75}	C(10)···H(14)	277.1(35)	16.5(tied to u_4)	0.3	17.3
u_5	P(1)···P(4)	279.1(4)	5.4(tied to u_4)	0.0	5.7
u_{86}	P(4)···H(19)	292.9(12)	26.0(tied to u_4)	4.6	24.1
u_{87}	Cl(6)···H(12)	297.8(47)	27.5(tied to u_4)	9.9	28.9
u_{91}	H(13)···H(19)	301.3(23)	28.4(fixed)	–0.7	28.4
u_{88}	P(1)···C(7)	302.9(8)	7.9(tied to u_{98})	–0.1	7.3
u_{95}	H(11)···H(17)	303.3(23)	28.3(fixed)	–0.8	28.3
u_{97}	H(13)···H(16)	303.9(22)	28.3(fixed)	–0.9	28.3
u_{93}	H(12)···H(15)	304.0(22)	28.7(fixed)	–0.7	28.7
u_{90}	P(4)···C(7)	304.7(3)	8.4(tied to u_{98})	–0.4	7.8
u_{92}	P(1)···H(16)	306.2(27)	23.0(tied to u_4)	5.0	24.2
u_{85}	P(5)···H(18)	306.6(27)	25.3(tied to u_{98})	5.4	23.5
u_{94}	H(15)···H(18)	307.0(36)	28.8(fixed)	–0.7	28.8
u_{89}	P(5)···C(7)	307.1(11)	8.5(tied to u_{98})	–0.1	7.9
u_{99}	P(1)···H(12)	307.6(22)	27.1(tied to u_{98})	3.7	25.1
u_{96}	H(14)···H(17)	309.0(35)	28.6(fixed)	–0.8	28.6
u_{100}	P(5)···H(14)	309.7(40)	39.8(tied to u_6)	3.7	28.4
u_{98}	C(3)···Cl(6)	312.9(6)	10.4(3)	–0.1	9.6
u_{118}	Cl(6)···H(11)	325.6(39)	67.6(tied to u_6)	2.6	48.1
u_{103}	P(4)···C(10)	330.0(16)	22.6(tied to u_6)	0.6	16.1
u_{115}	P(4)···H(18)	332.6(32)	47.5(tied to u_6)	–0.3	33.8

u_{101}	P(4)···H(11)	335.2(38)	30.7(tied to u_{98})	2.8	28.5
u_{105}	C(3)···H(15)	342.9(5)	14.2(tied to u_6)	–1.5	10.1
u_{106}	C(3)···H(13)	343.0(5)	14.2(tied to u_6)	–1.5	10.1
u_{108}	C(10)···H(12)	344.2(11)	14.2(tied to u_6)	–1.5	10.1
u_{109}	C(8)···H(18)	344.2(12)	14.3(tied to u_6)	–1.5	10.2
u_{107}	C(3)···H(17)	344.5(6)	14.2(tied to u_6)	–1.4	10.1
u_{112}	C(8)···H(14)	345.0(11)	14.3(tied to u_6)	–1.5	10.2
u_{111}	C(9)···H(11)	345.0(11)	14.3(tied to u_6)	–1.5	10.2
u_{104}	P(1)···C(9)	345.6(21)	18.1(tied to u_{98})	0.9	16.8
u_{110}	C(10)···H(16)	347.1(17)	14.3(tied to u_6)	–1.5	10.2
u_{116}	P(1)···C(8)	347.1(19)	24.3(tied to u_6)	0.2	17.3
u_{113}	C(9 ···H(19)	347.2(17)	14.3(tied to u_6)	–1.5	10.2
u_{102}	P(5)···C(10)	347.7(20)	22.4(tied to u_6)	1.1	16.0
u_6	P(4)···Cl(6)	348.6(13)	20.7(5)	0.0	14.7
u_{117}	P(5)···C(9)	353.4(33)	27.5(tied to u_6)	0.1	19.6
u_{121}	Cl(6)···C(8)	353.4(31)	30.2(tied to u_6)	3.2	21.5
u_{119}	P(1)···H(14)	362.0(30)	49.0(tied to u_6)	–0.4	34.9
u_{114}	P(5)···H(19)	365.5(34)	48.3(tied to u_6)	–0.1	34.4
u_{135}	P(1)···H(11)	366.6(27)	45.9(tied to u_6)	–1.5	32.7
u_{132}	H(12)···H(19)	368.4(24)	17.9(fixed)	–1.8	17.9
u_{133}	H(11)···H(18)	368.6(24)	17.9(fixed)	–1.8	17.9
u_{129}	H(12)···H(14)	369.0(23)	17.8(fixed)	–1.9	17.8
u_{128}	H(11)···H(16)	369.1(23)	17.9(fixed)	–1.8	17.9
u_{120}	P(4)···C(8)	370.1(25)	26.7(tied to u_6)	–0.5	19.0
u_{123}	H(13)···H(18)	370.7(18)	17.5(fixed)	–1.6	17.5
u_{122}	H(12)···H(17)	370.8(18)	17.5(fixed)	–1.6	17.5
u_{127}	H(13)···H(14)	372.6(18)	17.8(fixed)	–1.7	17.8
u_{126}	H(11)···H(15)	372.7(18)	17.7(fixed)	–1.7	17.7
u_{124}	H(16)···H(17)	373.3(25)	17.7(fixed)	–1.7	17.7
u_{125}	H(15)···H(19)	373.3(25)	17.7(fixed)	–1.6	17.7
u_{131}	H(16)···H(18)	374.5(35)	17.9(fixed)	–1.9	17.9
u_{130}	H(14)···H(19)	374.8(35)	17.9(fixed)	–1.7	17.9
u_{134}	C(3)···C(20)	379.5(4)	9.0(tied to u_6)	–0.3	6.4
u_{136}	P(5)···H(16)	379.7(37)	34.9(tied to u_7)	–1.8	34.0
u_{137}	Cl(6)···C(7)	394.7(20)	18.4(tied to u_6)	–0.3	13.1
u_{138}	P(4)···H(12)	400.6(33)	44.8(tied to u_6)	–2.2	31.9
u_{139}	Cl(6)···H(16)	421.3(60)	60.2(tied to u_6)	2.0	42.8
u_{140}	P(4)···C(9)	425.7(9)	9.0(tied to u_7)	–2.1	8.7
u_{144}	H(12)···H(18)	426.1(14)	13.3(fixed)	–2.5	13.3
u_{142}	H(11)···H(14)	426.3(14)	13.4(fixed)	–2.6	13.4
u_{145}	H(16)···H(19)	427.1(16)	13.3(fixed)	–2.5	13.3
u_{141}	P(1)···C(10)	428.5(7)	8.3(tied to u_7)	–1.9	8.1
u_{149}	P(4)···H(14)	430.6(22)	19.9(tied to u_7)	–2.0	19.4
u_{143}	P(5)···C(8)	432.8(5)	9.1(tied to u_7)	–2.0	8.8
u_{147}	P(4)···H(17)	435.5(12)	17.1(tied to u_7)	–2.0	16.6
u_7	P(5)···Cl(6)	443.1(5)	8.3(4)	–0.6	8.1

u_{152}	C(3)···H(25)	444.3(9)	23.3(tied to u_7)	–0.1	22.7
u_{160}	C(3)···H(29)	444.5(20)	21.9(tied to u_7)	–0.3	21.3
u_{151}	C(3)···H(24)	444.5(14)	23.6(tied to u_7)	0.3	22.9
u_{156}	C(3)···H(27)	444.7(19)	23.2(tied to u_7)	0.0	22.6
u_{148}	P(1)···H(15)	446.4(19)	17.3(tied to u_7)	–1.7	16.8
u_{162}	P(1)···H(19)	446.6(10)	17.2(tied to u_7)	–2.6	16.8
u_{153}	P(1)···H(18)	447.1(18)	18.6(tied to u_7)	–2.1	18.1
u_{150}	P(5)···H(11)	448.2(19)	20.1(tied to u_7)	–2.2	19.6
u_{161}	P(1)···H(13)	448.5(16)	17.3(tied to u_7)	–1.9	16.9
u_{146}	P(5)···H(17)	448.9(18)	16.8(tied to u_7)	–1.5	16.4
u_{157}	C(3)···H(31)	449.0(12)	22.5(tied to u_7)	0.6	21.9
u_{154}	C(3)···H(32)	449.0(16)	22.0(tied to u_7)	0.8	21.4
u_{155}	C(3)···C(21)	452.3(6)	10.8(tied to u_7)	–0.6	10.5
u_{159}	C(3)···C(22)	452.4(13)	10.4(tied to u_7)	–0.8	10.1
u_{167}	Cl(6)···H(13)	453.2(35)	23.5(tied to u_7)	–0.5	22.9
u_{163}	P(5)···H(15)	453.4(29)	19.5(tied to u_7)	–2.0	19.0
u_{166}	P(5)···H(12)	453.5(12)	17.0(tied to u_7)	–2.9	16.5
u_{164}	P(4)···H(16)	453.9(9)	17.2(tied to u_7)	–2.9	16.8
u_{158}	C(3)···C(23)	455.6(9)	10.0(tied to u_7)	–0.2	9.8
u_{165}	P(4)···H(13)	466.4(21)	19.4(tied to u_7)	–2.4	18.9
u_{168}	Cl(6)···C(9)	472.3(40)	29.2(tied to u_7)	–1.6	28.4
u_{174}	Cl(6)···H(19)	499.0(29)	31.1(tied to u_{173})	–2.5	32.4
u_{169}	P(4)···H(15)	511.2(8)	11.4(tied to u_{173})	–3.1	11.9
u_{170}	P(1)···H(17)	513.0(10)	11.1(tied to u_{173})	–2.7	11.6
u_{173}	Cl(6)···C(10)	514.3(15)	16.9(9)	–2.9	17.7
u_{171}	P(5)···H(13)	517.1(10)	11.6(tied to u_{173})	–2.8	12.1
u_{172}	Cl(6)···H(14)	527.7(36)	37.0(tied to u_{173})	–5.0	38.7
u_8	C(7)···C(20)	532.5(6)	6.9(tied to u_{173})	–0.8	7.2
u_{175}	Cl(6)···H(15)	550.8(43)	26.9(tied to u_{173})	–2.8	28.1
u_{176}	C(3)···H(26)	555.4(6)	17.3(tied to u_{191})	–2.8	12.1
u_{178}	C(3)···H(28)	555.9(12)	11.3(tied to u_{191})	–2.8	11.8
u_{14}	H(12)···H(29)	558.0(68)	35.8(fixed)	6.0	35.8
u_{11}	H(16)···H(25)	558.1(15)	39.6(fixed)	7.5	39.6
u_{177}	C(3)···H(30)	558.1(7)	16.7(tied to u_{191})	–2.4	11.6
u_{13}	H(11)···H(27)	558.2(63)	39.2(fixed)	6.7	39.2
u_9	H(14)···H(24)	558.7(51)	39.8(fixed)	9.0	39.8
u_{179}	Cl(6)···H(18)	566.9(12)	28.4(tied to u_{191})	–5.3	19.7
u_{12}	H(19)···H(31)	567.9(25)	38.0(fixed)	8.1	38.0
u_{10}	H(18)···H(32)	568.4(57)	36.3(fixed)	9.1	36.3
u_{182}	H(14)···H(25)	581.8(26)	48.6(fixed)	3.7	48.6
u_{193}	H(11)···H(29)	581.9(62)	45.4(fixed)	2.0	45.4
u_{183}	C(7)···H(25)	582.0(9)	35.9(tied to u_{191})	–0.5	25.0
u_{180}	C(7)···H(24)	582.2(22)	36.0(tied to u_{191})	0.2	25.1
u_{186}	C(7)···H(27)	582.3(31)	35.3(tied to u_{191})	–0.6	24.5
u_{187}	C(7)···H(29)	582.3(33)	33.0(tied to u_{191})	–0.9	23.0
u_{190}	Cl(6)···H(17)	585.7(20)	28.6(tied to u_{191})	–3.3	19.9

u_{184}	C(7)···H(31)	586.8(12)	34.5(tied to u_{191})	0.2	24.0
u_{181}	C(7)···H(32)	587.0(24)	33.4(tied to u_{191})	0.6	23.2
u_{185}	H(18)···H(31)	591.3(35)	45.9(fixed)	4.2	45.9
u_{188}	C(7)···C(21)	598.8(8)	17.5(tied to u_{191})	–1.1	12.2
u_{191}	C(7)···C(22)	598.9(23)	16.5(10)	–1.5	11.5
u_{195}	C(9)···H(25)	600.3(14)	47.3(tied to u_{191})	2.8	32.9
u_{192}	C(9)···H(24)	600.6(36)	47.2(tied to u_{191})	3.6	32.9
u_{197}	C(8)···H(27)	600.6(55)	45.5(tied to u_{191})	2.0	31.6
u_{199}	C(8)···H(29)	600.7(58)	42.7(tied to u_{191})	1.5	29.7
u_{189}	C(7)···C(23)	602.2(11)	16.1(tied to u_{191})	–0.7	11.2
u_{201}	H(12)···H(25)	605.9(38)	36.0(fixed)	2.6	36.0
u_{196}	C(10)···H(31)	609.1(24)	44.4(tied to u_{191})	3.4	30.9
u_{194}	C(10)···H(32)	609.4(42)	43.0(tied to u_{191})	3.9	29.9
u_{200}	H(11)···H(31)	610.1(35)	38.6(fixed)	3.3	38.6
u_{198}	H(14)···H(32)	614.6(48)	38.3(fixed)	4.8	38.3
u_{15}	C(9)···C(21)	630.8(21)	28.0(tied to u_{191})	1.0	19.5
u_{17}	C(8)···C(22)	630.8(49)	25.7(tied to u_{191})	–0.1	17.9
u_{16}	C(10)···C(23)	638.7(28)	17.0(tied to u_{215})	1.4	17.0
u_{206}	C(8)···H(25)	647.4(26)	39.0(tied to u_{191})	–1.2	27.2
u_{207}	C(9)···H(29)	647.6(28)	38.7(tied to u_{191})	–1.1	26.9
u_{204}	C(10)···H(27)	651.4(25)	28.9(tied to u_{215})	–0.9	29.0
u_{205}	C(8)···H(31)	653.0(24)	28.2(tied to u_{215})	–0.5	28.3
u_{202}	C(10)···H(24)	654.2(33)	29.0(tied to u_{215})	0.1	29.1
u_{203}	C(9)···H(32)	655.8(33)	28.4(tied to u_{215})	0.4	28.5
u_{212}	H(11)···H(25)	661.2(32)	36.6(fixed)	–3.8	36.6
u_{213}	H(12)···H(24)	661.2(20)	37.7(fixed)	–3.3	37.7
u_{211}	H(11)···H(32)	665.1(20)	37.8(fixed)	–3.0	37.8
u_{216}	H(12)···H(31)	665.2(33)	36.8(fixed)	–3.2	36.8
u_{209}	H(16)···H(32)	668.4(26)	39.2(fixed)	–2.5	39.2
u_{208}	H(14)···H(31)	668.6(28)	38.4(fixed)	–2.4	38.4
u_{215}	C(8)···C(21)	676.8(17)	15.7(9)	–2.8	15.7
u_{214}	C(8)···C(23)	679.9(16)	16.4(tied to u_{215})	–2.4	16.4
u_{219}	C(8)···H(24)	680.7(13)	27.1(tied to u_{215})	–3.6	27.2
u_{220}	C(9)···H(27)	680.8(24)	26.3(tied to u_{215})	–3.9	26.4
u_{210}	C(9)···C(23)	681.5(19)	17.1(tied to u_{215})	–1.9	17.2
u_{222}	C(10)···H(29)	683.0(24)	25.7(tied to u_{215})	–4.1	25.8
u_{217}	C(10)···H(25)	684.2(11)	28.1(tied to u_{215})	–3.7	28.2
u_{221}	C(8)···H(32)	684.9(13)	26.1(tied to u_{215})	–3.2	26.2
u_{218}	C(9)···H(31)	686.3(13)	27.1(tied to u_{215})	–3.2	27.2
u_{227}	H(11)···H(24)	693.1(16)	30.5(fixed)	–6.0	30.5
u_{232}	H(12)···H(32)	697.2(16)	29.2(fixed)	–5.5	29.2
u_{228}	H(16)···H(31)	697.6(14)	31.0(fixed)	–5.5	31.0
u_{223}	C(7)···H(26)	704.0(7)	13.4(tied to u_{215})	–3.6	13.5
u_{225}	C(7)···H(28)	704.3(21)	12.8(tied to u_{215})	–3.7	12.9
u_{224}	C(7)···H(30)	707.0(9)	12.7(tied to u_{215})	–3.2	12.8
u_{230}	H(15)···H(25)	707.9(14)	34.1(fixed)	–0.8	34.1

u_{234}	H(12)···H(28)	708.3(59)	30.7(fixed)	–1.7	30.7
u_{226}	H(14)···H(26)	708.3(39)	34.0(fixed)	0.0	34.0
u_{233}	H(11)···H(28)	708.4(56)	32.7(fixed)	–1.5	32.7
u_{231}	H(17)···H(31)	716.8(24)	32.1(fixed)	–0.1	32.1
u_{229}	H(17)···H(32)	717.0(44)	31.0(fixed)	0.5	31.0
u_{235}	C(9)···H(26)	738.6(21)	21.1(tied to u_{215})	–2.4	21.1
u_{237}	C(8)···H(28)	738.8(48)	19.4(tied to u_{215})	–3.2	19.4
u_{236}	C(10)···H(30)	745.9(27)	18.7(tied to u_{215})	–1.9	18.8
u_{243}	H(12)···H(26)	748.3(34)	27.4(fixed)	–3.6	27.4
u_{242}	H(13)···H(25)	748.3(24)	27.9(fixed)	–3.3	27.9
u_{241}	H(11)···H(30)	750.7(31)	29.7(fixed)	–3.1	29.7
u_{240}	H(13)···H(31)	753.0(22)	29.1(fixed)	–2.5	29.1
u_{238}	H(14)···H(30)	753.4(35)	29.8(fixed)	–1.8	29.8
u_{239}	H(15)···H(32)	755.3(36)	28.9(fixed)	–1.9	28.9
u_{254}	H(11)···H(26)	776.3(30)	27.6(fixed)	–5.8	27.6
u_{251}	H(13)···H(24)	776.5(16)	28.3(fixed)	–4.9	28.3
u_{255}	H(12)···H(30)	778.1(32)	26.9(fixed)	–5.4	26.9
u_{249}	C(8)···H(26)	778.1(21)	16.6(tied to u_{215})	–5.1	16.6
u_{247}	C(9)···H(28)	778.5(14)	16.6(tied to u_{215})	–4.6	16.7
u_{250}	H(16)···H(30)	779.3(12)	29.4(fixed)	–4.8	29.4
u_{248}	C(8)···H(30)	780.6(20)	17.4(tied to u_{215})	–4.7	17.4
u_{253}	H(13)···H(32)	780.9(17)	27.4(fixed)	–4.4	27.4
u_{246}	C(10)···H(28)	781.3(12)	17.4(tied to u_{215})	–4.5	17.4
u_{244}	C(9)···H(30)	781.9(18)	18.1(tied to u_{215})	–4.0	18.1
u_{252}	H(15)···H(31)	782.0(15)	28.3(fixed)	–4.7	28.3
u_{245}	C(10)···H(26)	782.4(19)	17.8(tied to u_{215})	–4.3	17.8
u_{18}	H(15)···H(26)	845.7(21)	22.6(fixed)	–5.8	22.6
u_{20}	H(13)···H(28)	846.2(48)	20.8(fixed)	–6.4	20.8
u_{19}	H(17)···H(30)	853.0(27)	20.3(fixed)	–5.2	20.3
u_{258}	H(13)···H(26)	881.0(18)	17.5(fixed)	–7.4	17.5
u_{257}	H(13)···H(30)	883.6(16)	18.4(fixed)	–6.9	18.4
u_{256}	H(15)···H(30)	884.6(18)	18.8(fixed)	–6.6	18.8

[a] Estimated standard deviations, as obtained in the least squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the force field calculated at the MP2/6-311+G* level.

Table S3 Least-squares correlation matrix (×100) for tricyclo-$P_3C_2(Bu^t)_2Cl$.[a]

	p_{10}	p_{11}	p_{12}	p_{16}	p_{17}	p_{18}	u_1	u_{23}	u_{36}	u_{85}	u_{102}	u_{134}	k_2
p_5			61		–52						65		
p_6					50								
p_7	–64	–92		–95	–61	51	–88						
p_8	–55				–50			52					
p_{10}		59		59			61						
p_{11}				90		–50	83						
p_{12}											54		
p_{13}						–52			–68			74	
p_{16}					65	–54	83						
p_{18}									63			–50	
u_{36}												–50	
u_{50}										50			62
u_{85}													83
u_{102}													54

[a] Only elements with absolute values ≥ 50% are shown.

Table S4 GED coordinates for tricyclo-$P_3C_2(Bu^t)_2Cl$.

Atom	*x*	*y*	*z*
P(1)	0.0000	–0.8114	1.1883
C(2)	1.1334	0.0000	0.0000
C(3)	–1.1334	0.0000	0.0000
P(4)	0.0000	–0.0137	–1.4873
P(5)	0.0000	1.5329	0.0000
Cl(6)	0.0000	–2.8736	0.5276
C(7)	–2.6669	0.0037	0.0000
C(8)	–3.1600	–1.4520	–0.1378
C(9)	–3.1550	0.5912	1.3409
C(10)	–3.1886	0.8219	–1.1999
H(11)	–2.7715	–1.8568	–1.0901
H(12)	–2.7719	–2.0282	0.7220
H(13)	–4.2653	–1.4410	–0.1370
H(14)	–2.7630	1.6211	1.4268
H(15)	–4.2603	0.5906	1.3332
H(16)	–2.7670	–0.0465	2.1560
H(17)	–4.2935	0.8054	–1.1716
H(18)	–2.8082	1.8551	–1.1016
H(19)	–2.8118	0.3506	–2.1260
C(20)	2.6669	0.0037	0.0000
C(21)	3.1550	0.5912	1.3409
C(22)	3.1600	–1.4520	–0.1378
C(23)	3.1886	0.8219	–1.1999
H(24)	2.7630	1.6211	1.4268
H(25)	2.7670	–0.0465	2.1560
H(26)	4.2603	0.5906	1.3332
H(27)	2.7715	–1.8568	–1.0901
H(28)	4.2653	–1.4410	–0.1370
H(29)	2.7719	–2.0282	0.7220
H(30)	4.2935	0.8054	–1.1716
H(31)	2.8118	0.3506	–2.1260
H(32)	2.8082	1.8551	–1.1016

Table S5 Calculated coordinates (MP2/6-311+G*) for tricyclo-$P_3C_2(Bu^t)_2Cl$.

Atom	*x*	*y*	*z*
P(1)	0.0000	–0.8949	0.9472
C(2)	1.1179	0.2522	0.0449
C(3)	–1.1179	0.2522	0.0449
P(4)	0.0000	0.6703	–1.4043
P(5)	0.0000	1.7271	0.5278
Cl(6)	0.0000	–2.6658	–0.2685
C(7)	–2.6318	0.2927	0.0450
C(8)	–3.1635	–0.8594	–0.8181
C(9)	–3.1335	0.1341	1.4840
C(10)	–3.1224	1.6247	–0.5303
H(11)	–2.8053	–0.7715	–1.8489
H(12)	–2.8410	–1.8299	–0.4325
H(13)	–4.2589	–0.8419	–0.8319
H(14)	–2.7504	0.9354	2.1249
H(15)	–4.2280	0.1679	1.5093
H(16)	–2.8175	–0.8236	1.9100
H(17)	–4.2170	1.6375	–0.5630
H(18)	–2.7952	2.4711	0.0827
H(19)	–2.7581	1.7802	–1.5516
C(20)	2.6318	0.2927	0.0450
C(21)	3.1335	0.1341	1.4840
C(22)	3.1635	–0.8594	–0.8181
C(23)	3.1224	1.6247	–0.5303
H(24)	2.7504	0.9354	2.1249
H(25)	2.8175	–0.8236	1.9100
H(26)	4.2280	0.1679	1.5093
H(27)	2.8053	–0.7715	–1.8489
H(28)	4.2589	–0.8419	–0.8319
H(29)	2.8410	–1.8299	–0.4325
H(30)	4.2170	1.6375	–0.5630
H(31)	2.7581	1.7802	–1.5516
H(32)	2.7952	2.4711	0.0827

Energy = –1872.87773 Hartrees (not corrected for ZPE).

Table S6 Interatomic distances (r_a / pm), refined and calculated amplitudes of vibration (u / pm) and distance corrections (k_{h1} / pm) for the SARACEN-restrained GED structure of P≡C–Bu^t.[a]

	Atom pair	r_a	u(exp.)[b]	k_{h1}	u(calc.)
u_2	C(4)–H(5)	108.92(14)	8.66(tied to u_1)	0.4	7.6
u_1	C(4)–H(6)	108.93(14)	8.63(14)	0.4	7.6
u_3	C(1)–C(3)	147.78(16)	5.34(tied to u_4)	0.1	4.8
u_4	C(3)–C(4)	154.10(7)	5.69(8)	0.1	5.1
u_5	C(1)–P(2)	154.90(10)	4.28(tied to u_4)	0.1	3.8
u_6	H(6)···H(7)	174.4(1)	12.3(fixed)	–0.1	12.3
u_7	H(5)···H(6)	175.6(6)	12.3(fixed)	0.0	12.3
u_8	C(3)···H(5)	217.5(3)	10.7(tied to u_9)	–0.2	10.7
u_9	C(3)···H(6)	218.9(3)	10.6(3)	–0.2	10.6
u_{10}	C(1)···C(4)	246.2(1)	7.4(1)	–0.1	7.2
u_{11}	C(4)···C(8)	251.6(2)	7.5(tied to u_{10})	–0.1	7.2
u_{12}	H(5)···H(11)	256.5(10)	24.0(fixed)	2.4	24.0
u_{13}	H(6)···H(10)	260.2(15)	23.9(fixed)	2.5	23.9
u_{14}	C(1)···H(6)	273.1(5)	14.7(3)	0.0	16.2
u_{15}	C(4)···H(11)	275.9(5)	14.9(tied to u_{14})	0.1	16.5
u_{16}	C(4)···H(10)	277.5(7)	14.8(tied to u_{14})	0.1	16.4
u_{17}	C(4)···H(14)	277.5(7)	14.8(tied to u_{14})	0.1	16.4
u_{18}	P(2)···C(3)	301.7(2)	6.0(2)	–1.0	5.2
u_{19}	H(5)···H(10)	309.7(10)	26.1(fixed)	–0.8	26.1
u_{20}	H(5)···H(14)	309.7(10)	26.1(fixed)	–0.8	26.1
u_{21}	C(1)···H(5)	340.0(3)	12.8(tied to u_{22})	–1.5	10.2
u_{22}	C(4)···H(9)	346.8(2)	12.9(5)	–1.4	10.2
u_{23}	H(5)···H(9)	375.2(6)	17.6(fixed)	–1.7	17.6
u_{24}	H(5)···H(15)	375.2(6)	17.6(fixed)	–1.7	17.6
u_{25}	H(6)···H(9)	376.8(5)	17.5(fixed)	–1.7	17.5
u_{26}	P(2)···C(4)	381.0(1)	11.3(1)	–1.4	11.4
u_{27}	P(2)···H(6)	385.1(7)	22.7(tied to u_{26})	–0.9	22.9
u_{28}	P(2)···H(7)	385.1(7)	22.7(tied to u_{26})	–0.9	22.9
u_{29}	H(6)···H(15)	432.4(5)	13.6(fixed)	–2.5	13.6
u_{30}	P(2)···H(5)	482.5(2)	13.14(8)	–3.5	12.3

[a] Estimated standard deviations, as obtained in the least squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the force field calculated at the MP2/6-311+G* level.

Table S7 Least-squares correlation matrix (×100) for P≡C–Bu^t.[a]

	p_2	p_5	u_{10}	k_2
p_1	–72			
p_3		53		
p_4				54
p_5		100	50	
u_1				62
u_4				77

[a] Only elements with absolute values ≥ 50% are shown; k_2 is a scale factor.

Table S8 GED coordinates for P≡C–Bu^t.

Atom	*x*	*y*	*z*
C(1)	0.0000	0.0000	0.0000
P(2)	–1.5496	0.0000	0.0000
C(3)	1.4787	0.0000	0.0000
C(4)	1.9908	–0.7273	1.2597
H(5)	3.0828	–0.7399	1.2815
H(6)	1.6443	–0.2444	2.1762
H(7)	1.6443	–1.7624	1.2998
C(8)	1.9908	1.4545	0.0000
H(9)	1.6443	2.0068	–0.8764
H(10)	1.6443	2.0068	0.8764
H(11)	3.0828	1.4797	0.0000
C(12)	1.9908	–0.7273	–1.2597
H(13)	3.0828	–0.7399	–1.2815
H(14)	1.6443	–1.7624	–1.2998
H(15)	1.6443	–0.2444	–2.1762

Table S9 Calculated coordinates (MP2/6-311+G*) for P≡C–Bu^t.

Atom	*x*	*y*	*z*
C(1)	0.0000	0.0000	0.7354
P(2)	0.0000	0.0000	2.3063
C(3)	0.0000	0.0000	–0.7358
C(4)	1.2584	0.7266	–1.2381
H(5)	1.2704	0.7335	–2.3336
H(6)	1.2774	1.7612	–0.8842
H(7)	2.1639	0.2256	–0.8843
C(8)	–1.2584	0.7266	–1.2381
H(9)	–2.1639	0.2257	–0.8842
H(10)	–1.2774	1.7612	–0.8843
H(11)	–1.2704	0.7334	–2.3336
C(12)	0.0000	–1.4531	–1.2381
H(13)	0.0000	–1.4669	–2.3336
H(14)	0.8865	–1.9869	–0.8842
H(15)	–0.8866	–1.9869	–0.8843

Energy = –536.13417 Hartrees (not corrected for ZPE).

Table S10 Calculated coordinates (MP2/6-311+G*) for **3**.

Atom	*x*	*y*	*z*
P(1)	-1.0855	0.9138	-0.1441
C(2)	0.0933	-0.1797	-1.0534
P(3)	1.6355	0.1938	0.0640
Cl(4)	-2.9509	-0.1222	-0.3180
C(5)	0.2010	-0.1223	-2.5779
C(6)	-1.1066	-0.6084	-3.2246
C(7)	0.4180	1.3439	-2.9852
C(8)	1.3709	-0.9422	-3.1266
H(9)	-1.3910	-1.6048	-2.8817
H(10)	-1.9370	0.0683	-3.0083
H(11)	-0.9788	-0.6399	-4.3125
H(12)	1.3742	1.7222	-2.6089
H(13)	0.4205	1.4252	-4.0774
H(14)	-0.3771	1.9916	-2.6041
H(15)	1.4963	-0.7187	-4.1916
H(16)	2.3130	-0.6956	-2.6253
H(17)	1.1952	-2.0149	-3.0397
P(18)	-0.0810	-0.2613	1.4487
C(19)	0.4331	-1.2536	-0.0467
C(20)	0.6784	-2.7628	-0.0523
C(21)	-0.3861	-3.4288	-0.9330
H(22)	-1.3895	-3.0898	-0.6562
H(23)	-0.2295	-3.2098	-1.9906
H(24)	-0.3436	-4.5168	-0.8090
C(25)	2.0900	-3.1470	-0.5128
H(26)	2.8360	-2.7543	0.1849
H(27)	2.1857	-4.2386	-0.5347
H(28)	2.3268	-2.7690	-1.5060
C(29)	0.5081	-3.2875	1.3807
H(30)	0.7323	-4.3593	1.4029
H(31)	1.1942	-2.7911	2.0760
H(32)	-0.5151	-3.1464	1.7405

Energy = –1872.85805 Hartrees (not corrected for ZPE).

Table S11 Calculated coordinates (MP2/6-311+G*) for **4**.

Atom	*x*	*y*	*z*
C(1)	-0.1811	-1.4160	-0.3459
C(2)	1.7208	0.6349	-0.0382
P(3)	-0.0211	0.3044	0.0648
P(4)	1.2550	-2.3468	-0.1313
P(5)	2.7301	-0.7562	0.1074
Cl(6)	-0.9909	1.4256	-1.4136
C(7)	2.2888	2.0532	0.0267
C(8)	2.4389	2.5703	-1.4161
C(9)	1.3653	2.9856	0.8258
C(10)	3.6695	2.0711	0.6945
H(11)	3.1267	1.9314	-1.9791
H(12)	1.4824	2.5950	-1.9418
H(13)	2.8484	3.5870	-1.4012
H(14)	1.2262	2.6145	1.8458
H(15)	1.8157	3.9823	0.8846
H(16)	0.3835	3.0976	0.3598
H(17)	4.0431	3.1002	0.7252
H(18)	3.6172	1.6930	1.7203
H(19)	4.3991	1.4694	0.1451
C(20)	-1.5391	-2.0744	-0.5926
C(21)	-2.6555	-1.3501	0.1752
C(22)	-1.8223	-2.0246	-2.1056
C(23)	-1.5362	-3.5424	-0.1478
H(24)	-2.4527	-1.3525	1.2506
H(25)	-2.7817	-0.3155	-0.1524
H(26)	-3.6074	-1.8654	0.0071
H(27)	-1.0502	-2.5726	-2.6549
H(28)	-2.7908	-2.4938	-2.3136
H(29)	-1.8515	-0.9999	-2.4812
H(30)	-2.5224	-3.9795	-0.3371
H(31)	-0.7992	-4.1361	-0.6960
H(32)	-1.3199	-3.6307	0.9214

Energy = –1872.85295 Hartrees (not corrected for ZPE).

Table S12 Calculated coordinates (MP2/6-311+G*) for **5**.

Atom	*x*	*y*	*z*
C(1)	0.3586	0.0727	-1.2306
P(2)	-0.5619	0.9442	0.0035
P(3)	1.9490	-0.3520	-0.7135
Cl(4)	-2.5393	0.2780	0.0407
P(5)	-0.0785	-0.0134	-2.6902
C(6)	-0.9534	-1.2705	-2.8498
C(7)	-0.8815	1.2328	-3.0926
C(8)	1.1249	-0.1325	-3.6336
C(9)	-0.3871	-2.1668	-2.5776
H(10)	-1.8464	-1.2237	-2.2229
H(11)	-1.2730	-1.3685	-3.8939
H(12)	-0.2921	2.1415	-2.9362
H(13)	-1.1473	1.1737	-4.1536
H(14)	-1.8121	1.3220	-2.5259
H(15)	0.7700	-0.1951	-4.6678
H(16)	1.7830	0.7379	-3.5482
H(17)	1.7162	-1.0301	-3.4301
P(18)	0.3558	0.3318	1.8578
C(19)	1.8052	-0.1748	1.0717
C(20)	3.0606	-0.4795	1.8963
C(21)	2.7531	-0.5702	3.3947
H(22)	2.0068	-1.3440	3.6042
H(23)	3.6666	-0.8282	3.9405
H(24)	2.3855	0.3799	3.7938
C(25)	3.6615	-1.8216	1.4480
H(26)	3.9972	-1.7980	0.4076
H(27)	4.5303	-2.0626	2.0705
H(28)	2.9303	-2.6295	1.5544
C(29)	4.0839	0.6470	1.6738
H(30)	4.3765	0.7187	0.6217
H(31)	3.6652	1.6109	1.9809
H(32)	4.9863	0.4579	2.2667

Energy = –1872.85447 Hartrees (not corrected for ZPE).

Figure S1 Experimental and difference (experimental minus theoretical) molecular-scattering intensities for tricyclo-$P_3C_2(Bu^t)_2Cl$.

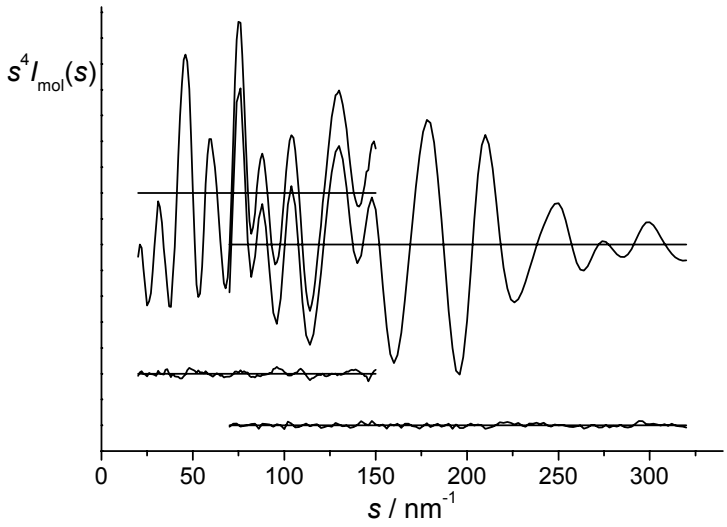

Figure S2 Experimental and difference (experimental minus theoretical) molecular-scattering intensities for $P{\equiv}C–Bu^t$.