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Syntheses and X-ray Structures of (Diphenylpyridylmethyl)lithium, -sodium, and -potassium in Comparison with the Triphenylmethyl Derivatives

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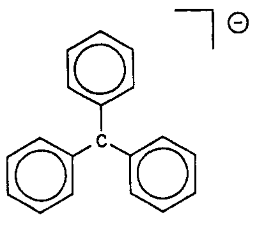
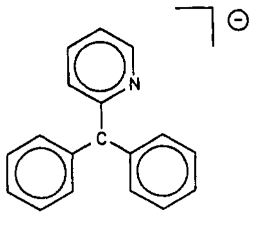
The crystal structures of $Ph_2CPyLi\cdot 2OEt_2$, $Ph_2CPyNa\cdot 3THF$, and $Ph_2CPyK\cdot PMDTA/THF$ (Py = pyridyl, THF = tetrahydrofuran, PMDTA = $(Me_2NCH_2Ch_2)_2NMe$) have been determined by low-temperature X-ray analysis. Whereas the potential energy surface of the triphenylmethyl alkali metal derivatives seems to be quite flat, that of the diphenylpyridylmethyl alkali metal compounds seems to have quite a distinct minimum. Structural features confirm the hypothesis that the negative charge is almost exclusively located at the nitrogen atom. Moreover, the results of the present study emphasize structural trends already established in the heavier triphenylmethyl alkali metal compounds.

Introduction

The preparation of molecules in more and more shallow depressions in the energy hyperface[1] (in terms of transition structures, reaction pathways, activation energies, etc.[2,3]), like the isolation of reaction intermediates[4,5] and highly thermolabile precursors,[6,7] makes it vital to elucidate the structure determining factors of such species in more detail. The lithium and sodium derivatives of the triphenylmethyl carbanion **a** have been structurally characterized by several workers,[8-11] and the potassium, rubidium, and cesium derivatives have been investigated recently.[12] The potential energy surface involving ions capable of delocalizing the negative charge to a maximum extent like in **a** is often quite flat.[2,13,14] We synthesized and determined the structures of the lithium, sodium, and potassium derivatives containing the diphenylpyridylmethyl carbanion **b**, to investigate the influence of a single nitrogen atom whithin one aromatic system on the structure and the coordinative behavior of the anion. The preparations and the structures of Ph_2PyCH (**1**), $Ph_2CPyLi\cdot 2OEt_2$ (**2**), $Ph_2CPyNa\cdot 3THF$ (**3**), and $Ph_2CPyK\cdot PMDTA/THF$ (**4**) are reported (Py = pyridyl, PMDTA = $(Me_2NCH_2CH_2)_2NMe$, THF = tetrahydrofuran).



a



b

Results and Discussion

Preparation of 2–4. Compound **2** was prepared by adding *n*-butyllithium to a diphenylpyridylmethane solution (eq 1). **3** and **4** were prepared according to eqs 2 and 3, respectively.

$$\underset{\mathbf{1}}{Ph_2PyCH} + {}^nBuLi \xrightarrow{-20\ ^\circ C\ \text{in}\ Et_2O} \underset{\mathbf{2}}{Ph_2CPyLi\cdot 2OEt_2} + {}^nBuH \quad (1)$$

$$\underset{\mathbf{1}}{Ph_2PyCH} + NaO^tBu + {}^nBuLi \xrightarrow{-30\ ^\circ C\ \text{in hexane/PMDTA/THF}} \underset{\mathbf{3}}{Ph_2CPyNa\cdot 3THF} + LiO^tBu + {}^nBuH \quad (2)$$

$$\underset{\mathbf{1}}{Ph_2PyCH} + KO^tBu + {}^nBuLi \xrightarrow{-30\ ^\circ C\ \text{in hexane/PMDTA/THF}} \underset{\mathbf{4}}{Ph_2CPyK\cdot PMDTA/THF} + LiO^tBu + {}^nBuH \quad (3)$$

In the syntheses of **3** and **4** the so-called "super bases"[15,16] have been employed because they are more reactive than, e.g., NaH or KH; hence it was possible to obtain the products at lower temperatures.

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Table I. Comparison of Geometrical Features (Distances in Picometers, Angles in Degrees)

	Ph_2PyCH (1)	$Ph_2CPy^-Li^+$ (2)	$Ph_2CPy^-Na^+$ (3)	$Ph_2CPy^-K^+$ (4)	$Ph_3C^-K^+$
donor		$(Et_2O)_2$	$(THF)_3$	PMDTA/THF	PMDTA/THF
C1–C2	152.2(3)	140.5(4)	142.7(7)	140.6(8)	143.5(5)
δ^a		12.9	20.3	18.6	17.7
C1–C7	151.8(3)	146.1(4)	146.3(6)	147.9(8)	147.5(6)
ϵ^b		32.2	25.9	43.5	40.2
C1–C13	152.6(3)	147.5(4)	147.9(6)	147.3(7)	146.0(6)
ϕ^a		46.2	42.7	34.0	31.1
C1 out of plane		0.7	2.5	0.3	1.0
metal–C1 distance		326.4(5)	349.6(10)	376.8(6)	404.8(4)
shortest metal–carbon distances		244.5(5) (C8)	285.9(9) C(7) 306.8(9) (C8)	314.0(6) (C8) 320.1(6) (C7) 345.5(7) (C9)	287.0(2)[d]
metal–N1 distance		197.2(5)	241.4(7)	280.9(5)	

[a] δ: angle between the C1–C2–C7–C13 plane and the Py plane. [b] ε: angle between the C1–C2–C7–C13 plane and the Ph1 plane. [c] ϕ: angle between the C1–C2–C7–C13 plane and the Ph2 plane. [d] K–Ph ring plane distance.

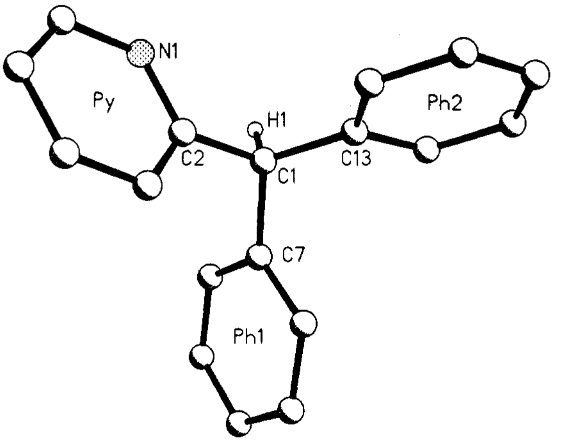

Figure 1. Structure of Ph_2PyCH (1) in the solid state.

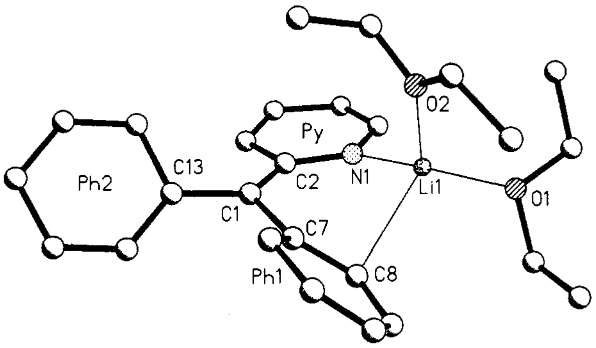

Figure 2. Structure of $Ph_2CPyLi{\cdot}2OEt_2$ (2) in the solid state.

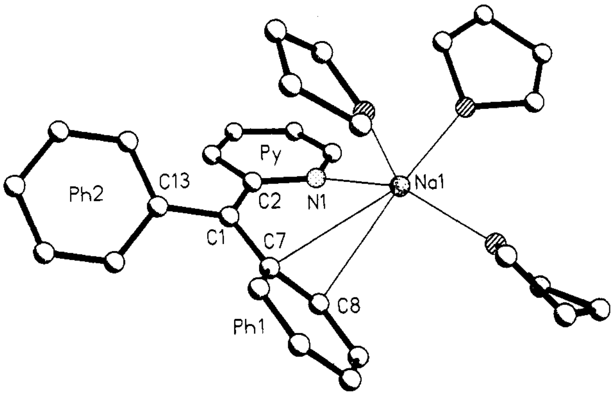

Figure 3. Structure of $Ph_2CPyNa{\cdot}3THF$ (3) in the solid state.

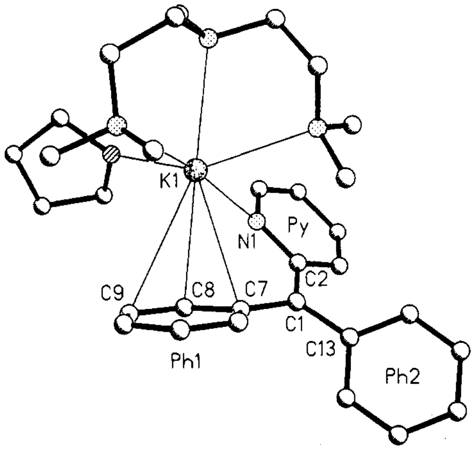

Figure 4. Structure of $Ph_2CPyK{\cdot}PMDTA/THF$ (4) in the solid state.

After 5 days in the refrigerator at 3 °C, X-ray suitable crystals have grown. They were mounted from the mother liquor onto the diffractometer. **3** crystallizes with three molecules of THF, although PMDTA is present in the solution.

Crystal Structure of 2. Unlike in the structure of $Ph_3CLi{\cdot}TMEDA$[8] (TMEDA = $Me_2NCH_2CH_2NMe_2$) and of $Ph_3CLi{\cdot}2OEt_2$,[9] there is no close contact of the lithium atom with the central carbon atom in **2** (C–Li: 222.7 pm in $Ph_3CLi{\cdot}TMEDA$, 230.6 pm in $Ph_3CLi{\cdot}2OEt_2$, and 326.4 pm in **2**). Even the shortest C–Li distance in **2** (Li1–C8: 244.5 pm; Figure 2, Table I) is on the average 15 pm longer than the shortest carbon–lithium contact in the triphenylmethyllithium contact ion pairs, therefore, too long to be considered as a bond.[17] However, the lithium atom is closely coordinated by the nitrogen atom of the pyridyl ligand. The Li1–N1 distance of 197.2 pm is in good accordance with lithium amides[18] and with those in the related species $(2\text{-}Me_3SiC(Li)Rpy)$(donor), R = H or $SiMe_3$.[19] The lithium atom in 1 is almost trigonally planar coordinated by the nitrogen atom and the two oxygen atoms of the two ether molecules (Li1 is only 48 pm above the N1–O1–O2 plane). At the same time it is only 42 pm pushed out of the plane of the pyridyl ligand. This explains

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Table II. Crystal Data for 1–4

	1	**2**	**3**	**4**
formula	$C_{18}H_{15}N$	$C_{26}H_{34}LiNO_2$	$C_{30}H_{38}NNaO_3$	$C_{31}H_{45}KN_4O$
fw	245.31	399.48	483.6	528.81
cryst size (mm)	0.6 × 0.6 × 0.8	0.2 × 0.2 × 0.5	0.3 × 0.3 × 0.5	0.3 × 0.4 × 0.5
space group	$P2_1/c$	Cc	$P6_5$	$P2_1/n$
a (pm)	825.6(6)	893.4(1)	997.0(5)	1692.5(5)
b (pm)	1501.7(11)	1724.6(1)	997.0(5)	1054.9(5)
c (pm)	1067.7(9)	1543.3(1)	4667.0(11)	1822.3(5)
α (deg)	90	90	90	90
β (deg)	93.24(6)	103.16(1)	90	112.29(3)
γ (deg)	90	90	120	90
V (nm^3)	1.321	2.315	4.018	3.010
Z	4	4	6	4
ρ_c (Mg m^{-3})	1.233	1.146	1.199	1.167
μ (mm^{-1})	0.07	0.07	0.09	0.21
F(000)	520	864	1560	1144
2θ range (deg)	8–45	8–53	8–50	8–48
no. of reflns measd	1867	4966	4705	5414
no. of unique reflns	1722	3970	4574	4863
no. of restraints	0	2	67	0
$wR2$ (all data)	0.112	0.106	0.181	0.219
$R1$ ($F > 4\sigma(F)$)	0.041	0.046	0.059	0.085
$g1$	0.062	0.031	0.071	0.070
$g2$	0.35	1.70	4.44	3.65
refined param	178	294	316	339
highest diff peak (10^{-6} e pm^{-3})	0.12	0.17	0.34	0.40

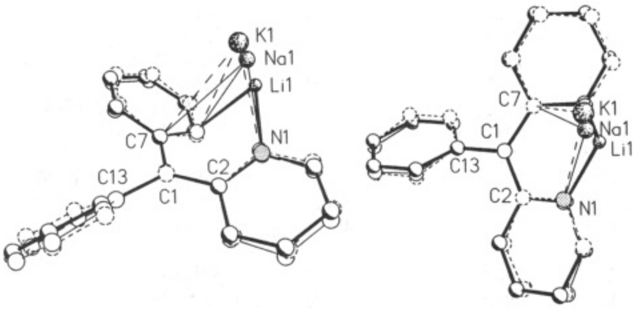

Figure 5. Superposition of the structures **2–4**, where the four central carbon atoms are fitted: (a) side view; (b) top view. Donor molecules have been omitted.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for Ph_2PyCH (1)

	x	y	z	U(eq)[a]
C(1)	3787(2)	324(1)	2658(2)	33(1)
H(1)	3289(22)	389(11)	3487(18)	37(5)
C(2)	3415(2)	1193(1)	1968(2)	32(1)
C(3)	4307(2)	1478(1)	974(2)	39(1)
C(4)	3888(2)	2250(1)	346(2)	46(1)
C(5)	2617(3)	2750(2)	718(2)	51(1)
C(6)	1773(3)	2458(2)	1700(2)	54(1)
N(1)	2150(2)	1685(1)	2329(2)	44(1)
C(7)	5599(2)	220(1)	2943(2)	34(1)
C(8)	6577(2)	−246(1)	2162(2)	42(1)
C(9)	8234(3)	−263(2)	2414(2)	52(1)
C(10)	8902(3)	165(2)	3450(2)	52(1)
C(11)	7913(3)	605(1)	4235(2)	49(1)
C(12)	6270(2)	640(1)	3989(2)	42(1)
C(13)	3013(2)	−487(1)	2004(2)	33(1)
C(14)	3191(2)	−1314(1)	2570(2)	46(1)
C(15)	2493(3)	−2064(2)	2032(2)	53(1)
C(16)	1598(2)	−2002(1)	902(2)	48(1)
C(17)	1422(2)	−1189(1)	327(2)	42(1)
C(18)	2120(2)	−435(1)	870(2)	35(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the contact to C8. It is caused by steric hindrance rather than by forming a bond. The ring at C7 forces the lithium atom out of the pyridyl plane.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for $Ph_2CPyLi(Et_2O)_2$ (2)

	x	y	z	U(eq)[a]
Li1	8351(5)	598(3)	−196(3)	30(2)
C1	6347(3)	−629.1(15)	−1607(2)	23.9(13)
C2	5790(3)	135(2)	−1718(2)	22.7(13)
C3	4360(3)	334(2)	−2311(2)	27.2(13)
C4	3833(3)	1075(2)	−2384(2)	31.5(13)
C5	4692(3)	1666(2)	−1889(2)	32.5(15)
C6	6059(3)	1454(2)	−1350(2)	29.4(15)
N1	6623(2)	731.1(13)	−1237.3(14)	25.9(12)
C7	7917(3)	−822.7(15)	−1142(2)	24.4(13)
C8	9198(3)	−355(2)	−1155(2)	27.2(14)
C9	10672(3)	−570(2)	−735(2)	34.3(14)
C10	10952(3)	−1257(2)	−271(2)	36.4(15)
C11	9724(3)	−1726(2)	−243(2)	35(2)
C12	8247(3)	−1516(2)	−662(2)	29.1(15)
C13	5321(3)	−1284(2)	−1952(2)	24.8(14)
C14	3840(3)	−1346(2)	−1824(2)	28.9(14)
C15	2884(3)	−1956(2)	−2154(2)	36.0(15)
C16	3388(4)	−2544(2)	−2615(2)	39(2)
C17	4864(4)	−2507(2)	−2752(2)	39(2)
C18	5815(3)	−1888(2)	−2425(2)	30.5(15)
O1	9732(2)	1487.0(11)	−12.2(12)	32.5(10)
C19	9600(4)	2195(2)	449(2)	44(2)
C20	8469(4)	2101(2)	1017(2)	49(2)
C21	10875(3)	1542(2)	−527(2)	38(2)
C(22)	12467(4)	1414(2)	16(2)	52(2)
O2	7645(2)	188.6(11)	794.5(11)	30.9(10)
C23	8575(30)	−306(9)	1510(15)	48(7)
C23′	8461(20)	−25(7)	1621(12)	40(4)
C24	10220(25)	−47(15)	1746(15)	68(10)
C24′	10134(19)	−11(9)	1625(11)	35(7)
C25	6020(3)	193(2)	757(2)	40.0(15)
C26	5312(4)	−589(2)	583(2)	54(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Crystal Structure of 3. Different from the sodium atom in $Ph_3CNa{\cdot}TMEDA$,[11] where it is placed almost central above the carbanion, the sodium atom in **3** is quite remarkably off-center (Figure 3). While the Na1–C1 distance to the central carbon atom in $Ph_3CNa{\cdot}TMEDA$ is 264.3 pm, it is 349.6 pm in **3** (Table I). Again, the sodium atom is almost exclusively coordinated by the nitrogen atom of the pyridyl ligand and by the oxygen atoms of the three THF molecules. The shortest Na–C distance (Na1–C8: 285.9 pm) is an indication for steric hindrance

Table V. Atomic Coordinates ($\times 10^4$) and equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$ for $Ph_2CPyNa(THF)_3$ (3)

	x	*y*	*z*	*U*(eq)[a]
Na1	8466(2)	7132(2)	9639.6(4)	40.9(9)
C1	8113(4)	4105(4)	9208.3(10)	29(2)
N1	6616(4)	5373(4)	9295.3(8)	34(2)
C2	6680(5)	4100(4)	9198.5(9)	30(2)
C3	5291(5)	2835(5)	9084.9(9)	31(2)
C4	3985(5)	2913(5)	9052.4(9)	33(2)
C5	3962(5)	4237(5)	9138.5(10)	37(2)
C6	5284(5)	5388(5)	9259.1(10)	37(2)
C7	9610(5)	5537(5)	9223.8(9)	32(2)
C8	9845(5)	6955(5)	9114.3(11)	40(2)
C9	11273(6)	8305(5)	9118.2(13)	53(3)
C10	12541(6)	8291(6)	9231.2(13)	57(3)
C11	12359(5)	6920(6)	9341.2(12)	50(2)
C12	10938(5)	5573(5)	9336.3(10)	38(2)
C13	8107(5)	2624(4)	9180.4(9)	30(2)
C14	7039(5)	1286(5)	9325.3(10)	37(2)
C15	6997(6)	–119(5)	9289.0(11)	44(3)
C16	7996(6)	–255(5)	9109.4(11)	46(3)
C17	9104(6)	1066(6)	8967.4(11)	42(3)
C18	9147(5)	2474(5)	8999.0(10)	35(2)
O1	8593(4)	5547(4)	9989.6(8)	56(2)
C19	7289(6)	4087(7)	10049(2)	111(5)
C20	7858(10)	3082(6)	10163(3)	138(10)
C21	9532(10)	3999(10)	10158(3)	176(10)
C22	9908(6)	5620(7)	10110(2)	84(4)
O2	10500(4)	9579(4)	9767.6(8)	57(2)
C23	11770(7)	9709(7)	9922.4(15)	78(4)
C24	13032(6)	11360(8)	9901(2)	109(4)
C25	12213(8)	12205(5)	9826.2(13)	94(6)
C26	10877(7)	11037(6)	9652.0(14)	74(4)
O3	6659(4)	7558(3)	9884.1(7)	50(2)
C27	5373(6)	6281(5)	10023.4(12)	58(3)
C28	4266(6)	6837(7)	10087.2(14)	77(4)
C29	5233(7)	8554(6)	10090(2)	84(6)
C30	6840(6)	8893(5)	10028.0(12)	58(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for $Ph_2CPyK{\cdot}PMDTA{\cdot}THF$ (4)

	x	*y*	*z*	*U*(eq)[a]
K1	3207.3(8)	8908.3(13)	1064.8(8)	35.0(6)
N1	4013(3)	9678(5)	2652(3)	36(3)
C1	4751(3)	11371(6)	2303(3)	31(3)
C2	4690(3)	10508(6)	2867(3)	31(3)
C3	5299(3)	10434(6)	3668(3)	34(3)
C4	5208(4)	9608(7)	4190(4)	39(3)
C5	4522(4)	8752(7)	3964(4)	49(4)
C6	3952(4)	8866(7)	3188(4)	45(3)
C7	4003(4)	11675(6)	1576(4)	33(3)
C8	3170(4)	11734(6)	1592(4)	38(3)
C9	2464(4)	11987(6)	898(4)	48(4)
C10	2542(4)	12203(6)	193(4)	48(4)
C11	3354(4)	12199(6)	169(4)	45(4)
C12	4060(4)	11930(6)	849(3)	35(3)
C13	5562(3)	12004(6)	2404(3)	31(3)
C14	6371(3)	11402(6)	2777(4)	35(3)
C15	7128(4)	12049(7)	2896(4)	44(3)
C16	7125(4)	13264(7)	2639(4)	45(4)
C17	6351(4)	13864(6)	2253(4)	47(4)
C18	5591(4)	13237(6)	2145(4)	39(3)
O1	1802(3)	8562(5)	1448(3)	60(3)
C19	1632(4)	9392(7)	1984(4)	55(4)
C20	725(5)	9763(9)	1600(6)	83(5)
C21	313(5)	8719(8)	1051(5)	66(4)
C22	1026(4)	7894(7)	1021(4)	55(4)
N2	4864(3)	7911(5)	1251(3)	36(3)
N3	3282(3)	6345(5)	478(3)	38(3)
N4	2302(3)	8430(5)	–580(3)	37(3)
C23	5316(4)	7612(7)	2089(4)	47(4)
C24	5317(4)	8936(7)	1046(4)	49(4)
C25	4807(4)	6802(6)	757(4)	48(3)
C26	4155(4)	5839(6)	799(4)	49(4)
C27	2753(5)	5699(7)	843(5)	63(5)
C28	2918(4)	6241(6)	–388(4)	46(4)
C29	2139(4)	7094(6)	–775(4)	44(4)
C30	1489(4)	9139(7)	–912(4)	58(4)
C31	2905(4)	8954(7)	–891(4)	54(5)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

again rather than a bond.[21] In 3 the sodium atom is forced 81 pm out of the pyridyl plane because of its bigger ionic radius compared to that of the lithium. The coordination sphere of the sodium atom is best described by a distorted tetrahedron consisting of one nitrogen atom and three oxygen atoms. The Na1–N distance of 241.4 pm is in good agreement with literature values.[22]

Crystal Structure of 4. In the $Ph_3CK{\cdot}PMDTA/THF$ contact ion pair the metal is placed almost above the center of one phenyl ring.[12] There is no bond between the central carbon and the potassium atom (404.8 pm, Table I). The ring center–metal distance is 287.1 pm. This distance falls at the short end of the range observed for other compounds with K–π system interactions.[23] $Ph_2CPyK{\cdot}PMDTA/THF$ adopts quite a different structure (Figure 4). As in 2 and 3 the relatively long K–C distances of 314.0–345.5 pm (to, e.g., dipotassium tetraphenylbutadienide,[24] 302–312 pm) indicate that the reason again is steric hindrance. The potassium metal is forced out of the plane of the pyridyl ligand by the remarkable amount of 110 pm. This interpretation would be in accordance with the structures of 2 and 3, but it is also possible to look at the potassium in 4 as being pulled out of the center of a phenyl ring in $Ph_3CK{\cdot}PMDTA/THF$ by being offered the quite attractive negative charge of the neighbor pyridyl ligand. But anyway, regardless of the interpretation one might favor, the potassium is "locked" in almost the same position as the lithium atom in 2 and the sodium atom in 3 (Figure 5). The K1–N1 distance (280.9 pm) is in good agreement with the value in related amides.[25]

Structural Comparison

Whereas the metal in the Ph_3C^- system seems to shift from the center of the anion (lithium and sodium) to the center of one of the phenyl rings (K, Rb, Cs),[12] the metal in the Ph_2PyC^- system seems to be interlocked at almost the same position, always going for the coordination of the nitrogen atom (Figure 5). The mesomeric formula depicted in c has considerable importance especially for M = K, Rb, Cs. These metals are η^6-coordinated to one phenyl ring. The bond between the central carbon atom and the ipso carbon atom of the coordinated ring is on average 2.4 pm shorter than the two others. Furthermore, the smallest torsion angle of the phenyl ring plane with

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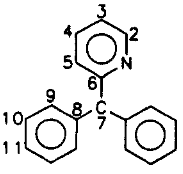
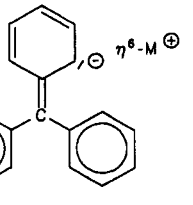
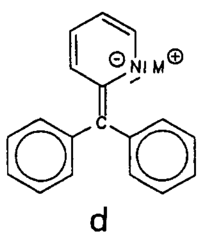
Table VII. ^1H and ^{13}C NMR Shifts (ppm) and Couplings (Hz) of **1** and of the Anions in **2–4**



	1		**2**		**3**		**4**	
position	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
2	8.45 (ddd, $^3J_{2,3}$ 4.8, $^4J_{2,4}$ 1.9, $^5J_{2,5}$ 0.9)	149.8 ($^1J_{2,3}$ 54.5)	7.18 (ddd, $^3J_{2,3}$ 5.4, $^4J_{2,4}$ 2.0, $^5J_{2,5}$ 1.0)	146.9	7.47 (ddd, $^3J_{2,3}$ 5.1, $^4J_{2,4}$ 2.1, $^5J_{2,5}$ 0.9)	148.1	7.16 (ddd, $^3J_{2,3}$ 5.3, $^4J_{2,4}$ 2.1, $^5J_{2,5}$ 1)	147.2
3	6.55 (ddd, $^3J_{3,4}$ 7.5, $^3J_{3,2}$ 4.8, $^4J_{3,5}$ 1.2)	121.2 ($^1J_{3,4}$ 54.4)	5.81 (ddd, $^3J_{3,2}$ 5.4, $^3J_{3,4}$ 6.5, $^4J_{3,5}$ 1.1)	105.9	5.93 (ddd, $^3J_{3,2}$ 5.1, $^3J_{3,4}$ 6.5, $^4J_{3,5}$ 1.1)	105.4	5.73 (ddd, $^3J_{3,2}$ 5.3, $^3J_{3,4}$ 6.3, $^4J_{3,5}$ 1)	103.1
4	6.98 (ddd, $^3J_{4,5}$ 7.9, $^3J_{4,3}$ 7.5, $^4J_{4,2}$ 1.9)	135.9 ($^1J_{4,5}$ 54.5)	6.64 (ddd, $^3J_{4,3}$ 6.5, $^3J_{4,5}$ 9.0, $^4J_{4,2}$ 2.0)	134.3	6.79 (ddd, $^3J_{4,3}$ 6.5, $^3J_{4,5}$ 8.9, $^4J_{4,2}$ 2.1)	133.8	6.60 (ddd, $^3J_{4,3}$ 6.3, $^3J_{4,5}$ 9.1, $^4J_{4,2}$ 2.1)	132.4
5	6.85 (ddd, $^3J_{5,4}$ 7.9, $^4J_{5,3}$ 1.2, $^5J_{5,2}$ 0.9)	123.8 ($^1J_{5,6}$ 58.2)	7.08 (ddd, $^3J_{5,4}$ 9.0, $^4J_{5,3}$ 1.1, $^5J_{5,2}$ 1.0)	118.9	7.29 (ddd, $^3J_{5,4}$ 8.9, $^4J_{5,3}$ 1.1, $^5J_{5,2}$ 0.9)	118.0	6.88 (ddd, $^3J_{5,4}$ 9.1, $^4J_{5,3}$ 1, $^5J_{5,2}$ 1)	119.5
6		163.6 ($^1J_{6,7}$ 50.0)		159.9		161.4		159.3
7	5.73 (s)	59.9 ($^1J_{7,8}$ 43.0)		93.9		94.0		97.0
8		143.6 ($^1J_{8,9}$ 58.5)		148.0		148.7		148.9
9	7.22 (m)	129.8 ($^1J_{9,10}$ 56.4)	7.72 (m)	127.5	7.84 (m)	127.6	7.82 (m)	128.0
10	7.09 (m)	128.6 ($^1J_{10,11}$ 55.9)	7.10 (m)	129.8	7.11 (m)	129.0	7.17 (m)	129.0
11	7.02 (m)	126.6 ($^1J_{10,11}$ 55.9)	6.74 (m)	120.2	6.70 (m)	118.7	6.83 (m)	119.6



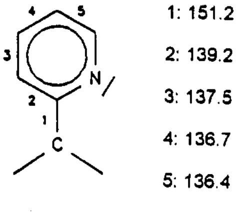
c



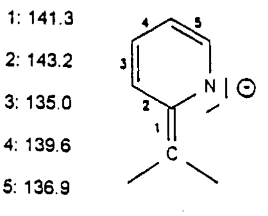
d

respect to the plane of the central carbon atom and the three ipso carbon atoms is found along the shortest C–C bond. Nevertheless, the two other phenyl groups are also present to delocalize the charge as well.

In **d** the ability to delocalize the charge in an optimum way is considerably distorted. The negative charge is almost exclusively located in the pyridyl ligand, especially at the nitrogen atom, reflected by the carbon–carbon distances:[26]



1



av. of 2 to 4

In **c** all carbon–carbon distances within the η^6-coordinated ring are equal. The difference between the central partial double bond and the two single bonds is emphasized by introducing the pyridyl ligand. The C–C bond between the central carbon atom and the ipso carbon atom of the pyridyl substituent is on average 5.5 pm shorter than the two others; hence the bond shortening caused by alkali metal coordination is 3 pm bigger than in the Ph_3CM, M = K, Rb, Cs, derivatives. The C–C distance between the central carbon and the ipso py carbon atom in $(Me_3Si)_2CHpy$ (150 pm) decreases to 142 pm in $(Me_3Si)_2C(Li)py$.[19] The exocyclic C–C distance in picolyllithium $[H_2CpyLi{\cdot}Et_2O]_2$ is 136.2(3) pm.[20] Moreover, in **2–4** the shortest central C–C bond is, as well as in the aforementioned systems, related to the smallest dihedral angle (Table I). Although planarity at C1 is not necessarily indicative for delocalization, the anisotropic displacement parameter of C1 in all structures does not show any disorder, which might be a hint at a very low inversion barrier. The average $C(sp^2)$–$C(sp^2)$ single bond is 146.6 pm,[27] hence 5 pm longer than the distance of the central carbon atom to the pyridyl ring. The shortening cannot be ascribed to the difference between a C–Py and a C–Ph bond. The three central bonds in **1** are all of the same length within their estimated standard deviation (average 152.2 pm; Table I). Even the central bonds in Ph_3CH and Py_3CH are of the same length (152(1) pm).[28]

Conclusion

Whereas the potential energy surface for the triphenylmethyl carbanion seems to be quite flat, there is quite a distinct minimum in that of the diphenylpyridylmethyl carbanion. This seems to be a carbanion only by formal means; the negative charge, however, is almost entirely located at the nitrogen atom. Nevertheless, the diphenylpyridylmethyl system emphasizes and extrapolates several structural features of the Ph_3C^- system and is therefore a valuable magnifying glass revealing small energetic differences.

Experimental Section

All manipulations were performed under an inert atmosphere of dry argon gas with Schlenk techniques or in an argon glovebox. The *n*-hexane, ether, and THF solvents were dried over Na/K alloy and distilled prior to use.

NMR spectra were obtained with a Bruker MSL 400 instrument. All NMR spectra were recorded in toluene-d_8 or benzene-d_6 with $SiMe_4$ or LiCl external reference.

$Ph_2CPyLi{\cdot}2OEt_2$ (2). To a solution of 1.23 g of Ph_2PyCH (5 mmol) in diethyl ether was added at −20 °C 3.2 mL of ^nBuLi in *n*-hexane (1.6 M solution, 5 mmol). The colorless solution turned dark red. Storage at +3 °C over a period of 4 weeks yielded dark

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[26] The same effect was found in the crystal structures of $HCPy_2Li{\cdot}2THF$, $[Li(Py_2CH)_2][Li(12\text{-crown-}4)_2]$, and $PPy_2Li{\cdot}2THF$: Gornitzka, H.; Steiner, A.; Stalke, D. To be published.

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red needles, suitable for X-ray structure analysis. Yield: 1.44 g (72%, first batch). Melting point: 60 °C. ^{1}H NMR (C_6D_6): δ 0.88, 3.10 (Et_2O). ^{7}Li NMR (C_6D_6): δ −0.19. ^{1}H and ^{13}C NMR shifts and couplings of the anion are listed in Table VII.

$Ph_2CPyNa·3THF$ (3). Ph_2PyCH (1.23 g, 5 mmol) and 0.44 g of NaO^tBu (5 mmol) were dissolved in 50 mL *n*-hexane. To the chilled solution (−30 °C) was added dropwise 3.2 mL of ^{n}BuLi in *n*-hexane (1.6 M solution, 5 mmol). After stirring for 1 h at −30 °C and 1 h at room temperature, THF was added dropwise until the precipitate redissolved and a clear dark red solution was obtained. Storage at +3 °C yielded red needles after 5 days. Yield: 1.84 g (76% first batch). Melting point: 115 °C. ^{1}H NMR (C_6D_6): δ 1.15, 3.26 (THF). ^{1}H and ^{13}C NMR shifts and couplings of the anion are shown in Table VII.

$Ph_2CPyK·PMDTA/THF$ (4). PhPyCH (0.98 g, 4 mmol) and 0.45 g KO^tBu (4 mmol) were dissolved in 50 mL of *n*-hexane, and the solution was chilled to −30 °C. Then 2.5 mL of ^{n}BuLi in *n*-hexane (1.6 M solution, 4 mmol) was added dropwise. The reaction mixture was stirred for 1 h at −30 °C and 2 h at room temperature. PMDTA (0.5 mL, 4 mmol) was added to the reaction mixture. THF was added dropwise until a clear dark red solution was obtained. Storage at +3 °C yielded dark red needles after 5 days. Yield: 1.77 g (84% first batch). Melting point: 105 °C. ^{1}H NMR (C_6D_6): δ 1.15, 3.25 (THF), 1.58, 1.85, 2.13 (PMDTA). ^{1}H and ^{13}C NMR shifts and couplings of the anion are shown in Table VII.

X-ray Measurements of 1–4

Crystal data of the four structures are presented in Table II. The data were collected at −120 °C on a Stoe-Siemens AED with Mo Kα (λ = 71.073 pm) radiation. The structures were solved by direct methods using SHELXS-90.[29] They were refined with all data on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g1P)^2 + g2P$ with $(P = (F_o^2 + 2F_c^2)/3$ using SHELXL-92.[30] The a priori assumed disordering of the nitrogen position in 1 over six possible positions could not be found in the structure. Astonishingly enough, the nitrogen atom is only disordered over two positions (Py and Ph2; Figure 1), and one of the two present ether molecules in 2 is disordered. The THF molecules of 3 were refined with restraints for equivalent 1–2 and 1–3 distances to improve the geometry. The absolute structures of 2 and 3 could not be reliably determined. The central methyl hydrogen of 1 was freely refined. All other hydrogen positions were refined by employing a riding model where the CH_3 groups were free to rotate about their local 3-fold axis. Selected bond lengths and angles of 1–4 can be found in Table I. The atomic coordinates of 1–4 are presented in Tables III to VI.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, and bond lengths and angles and labeled structures for 1–4 and tables of anisotropic thermal parameters and hydrogen atom positional parameters for 1 (19 pages). Ordering information is given on any current masthead page.

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