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Simple Access to α-Functional Phospholide Ions. 2. Application to the Synthesis of 1-Methyl-2-pyrrolyl and 2-(Diphenylphosphino)phenyl Derivatives

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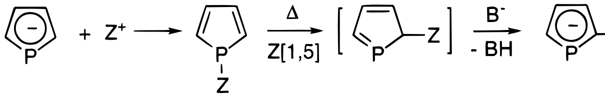
Heating 1-Z-3,4-dimethylphospholes with potassium *tert*-butoxide in THF at ca. 150−160 °C affords the corresponding potassium 2-Z-3,4-dimethylphospholides (Z = 1-methyl-2-pyrrolyl and 2-(diphenylphosphino)phenyl) via a [1,5]-sigmatropic shift of Z. The first anion can be used to prepare the corresponding bis(pyrrolyl)-1,1′-diphosphaferrocene, and the second anion is able to chelate palladium(II) between its phospholide and PPh_2 functionalities.

Introduction

Among the numerous carbon−phosphorus heterocycles which are presently known,[1] two of the simplest, i.e., the phospholide ion and phosphinine, play a special role as a result of their high aromaticity. The aromatic stabilization energy (ASE) of phosphinine has been evaluated at 88% of that of benzene,[2] whereas the ASE of the phospholide ion has been estimated between 90% and 100% of that of the cyclopentadienide ion.[3,4] Whereas the chemistry of phosphinines is now highly developed,[1,5,6] presently this is not the case for phospholide ions if we exclude coordination chemistry.[7] Indeed, all of the classical reagents react with these ions at phosphorus, and no chemistry at the carbons of the ring has been described until now. Very recently, we were able to devise the first simple access to α-functional phospholides[8] whose principle is depicted in eq 1.

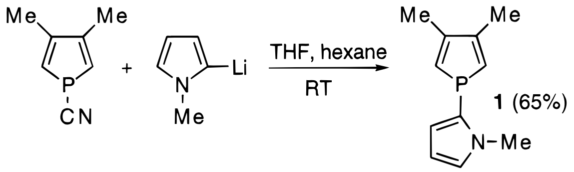


(1)

The two prerequisites for applying this scheme are a good migratory aptitude of Z—this is the case for sp^2-C, sp-C, Si, P, S...—and a good compatibility of Z with the base, generally ${}^tBuOK$, which is used to deprotonate the transient 2*H*-phosphole.[9] Three examples have been described in our preliminary communication, where Z stands for phenyl, 2-pyridyl, and ethoxycarbonyl. In fact the scope of this scheme is much broader. In this paper, we report on two additional examples of special interest for coordination chemists.

Results and Discussion

2-(1-Methyl-2-pyrrolyl)-3,4-dimethylphospholide. The starting product was 1-(1-methyl-2-pyrrolyl)-3,4-dimethylphosphole (**1**) prepared from 1-methyl-2-lithiopyrrole and 1-cyano-3,4-dimethylphosphole[10] as shown in eq 2. The two most noteworthy spectral features of **1** are its ^{31}P NMR resonance at high field $\delta^{31}P$ (**1**) −32 vs −2.5 for the P−Ph analogue, and the large coupling of the β carbon in the pyrrole ring with the phosphole P. An unambiguous assignment of the corresponding resonance was made using $^1H-^{13}C$ correlated spectra. The $^2J(C-P)$ value of 37.8 Hz can be compared with 18.3 Hz for the *o*-C_6H_5 carbon in the P−Ph analogue.[11] This high value suggests that the pyrrole ring is lying almost perpendicular to the phosphole plane with a Cβ−Cα−P−lone pair dihedral angle close to 0°.[12] The [1,5] shift of the pyrrole substituent around the phosphole ring proved to be rather difficult. The migration needs 3 days at 160 °C to go to completion. Under such extreme conditions, the resulting



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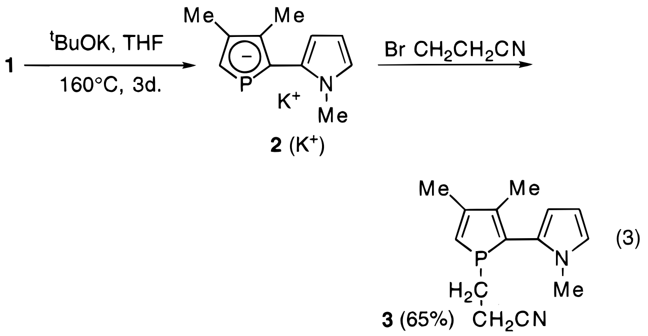
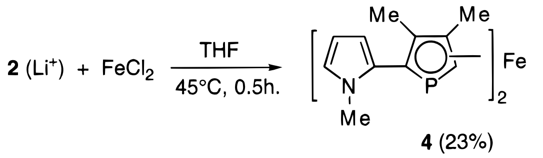
phospholide was nevertheless obtained in ≥65% yield, as measured on its alkylation product **3** (eq 3). This



(3)

satisfactory result emphasizes the extraordinary thermal stability of phospholide ions. From **3**, it is possible to get back **2** by treatment with a base (^{t}BuOK, BuLi) or a metal (Na). We have observed a significant variation of the ^{31}P shift of **2** with the nature of the counterion: δ^{31}P 74 (K$^+$), 61.7 (Na$^+$), and 56.5 (Li$^+$) in THF. This phenomenon suggests that the structure of **2** involves a more or less labile coordination of the pyrrole nitrogen with the counterion. The reaction of **2** with FeCl$_2$ affords, as expected,[13] the corresponding 1,1′-diphosphaferrocene **4** as a mixture of meso and rac diastereomers (eq 4).



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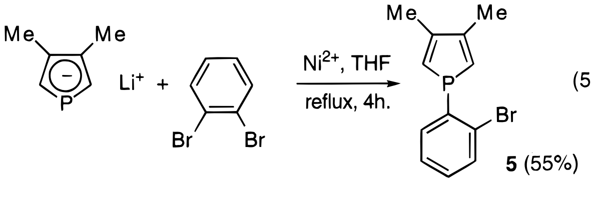
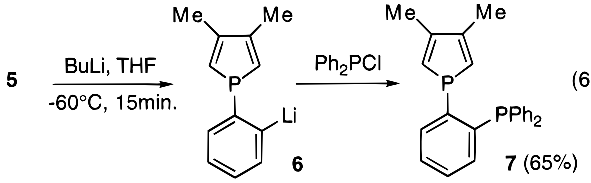
The major meso diastereomer displays a simple first-order ^{1}H NMR spectrum, and its ^{31}P resonance appears at −55.7 in CD$_2$Cl$_2$. The minor rac diastereomer displays a complex second-order ^{1}H NMR spectrum, and its phosphorus resonates at −57.8. Due to its two pyrrole rings, **4** might be incorporated into polypyrrole macrocycles and oligomers. Finally, it must be mentioned here that previous attempts to build the α-linked pyrrole−phosphole subunit failed.[14]

2-[2-(Diphenylphosphino)phenyl]-3,4-dimethylphospholide. Here our aim was to incorporate the phospholide ion into a chelating diphosphorus ligand. In the first step, 3,4-dimethylphospholide was allowed to react with 1,2-dibromobenzene. Even in the presence of a nickel catalyst, only the monosubstitution product was observed (eq 5).



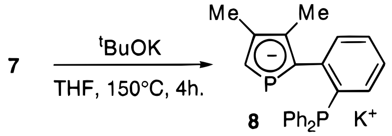
(5)

Bromine to lithium exchange readily takes place when **5** is allowed to react with butyllithium in THF at low temperature. The resulting *o*-lithiophenyl derivative **6** was then reacted with diphenylchlorophosphine to give **7** (eq 6).



(6)

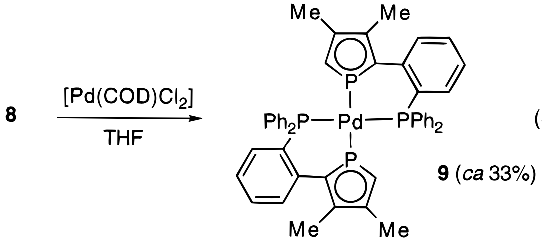
The diphosphine **7** displays a huge ^3J(P−P) coupling (110 Hz) which is characteristic of a cis P−C=C−P link.[15] When compared to the pyrrole case, the phosphinophenyl substituent of **7** migrates under less drastic conditions (eq 7).



(7)

The phospholide ion **8** is thus obtained almost quantitatively as monitored by ^{31}P analysis of the crude reaction mixture. The ^{31}P NMR data of **8** are highly characteristic: δ^{31}P (THF) +86.2 (P$^-$), −14.7 (PPh$_2$), ^4J(P−P) = 25 Hz. The anion was also characterized by negative-ion mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. The phospholide C$_2$ resonance occurs at 148.96 as a doublet of doublets: ^1J(C−P) = 40.8 Hz and ^3J(C−P) = 9 Hz. The strong ^1J(C−P) coupling is a constant feature of the phospholide ions.[16]

In order to demonstrate the chelating ability of this species, **8** was allowed to react with (cyclooctadiene)-palladium dichloride (eq 8). Unfortunately, we were unable to crystallize complex **9**, but its formulation was unambiguously established by a combination of NMR spectroscopy and mass spectrometry, including a comparison between the observed and simulated isotopic patterns of the molecular ion. The A$_2$X$_2$ ^{31}P spectrum of **9** implies that the geometry of this square-planar Pd(II) complex is trans. The availability of phospholide ions such as **2** and **8** offers numerous synthetic possibilities that we are currently exploring.



(8)

Experimental Section

All reactions were routinely performed under an inert atmosphere of nitrogen by using Schlenk techniques and dry deoxygenated solvents. Nuclear magnetic resonance spectra were obtained at 25 °C on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01

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MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in hertz. Mass spectra were obtained at 70 eV with an HP 5989 B spectrometer coupled with a HP 5890 chromatograph by the direct inlet method. The following abreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Elemental analyses were performed by the Service d'analyse du CNRS at Gif sur Yvette, France.

1-(1-Methyl-2-pyrrolyl)-3,4-dimethylphosphole (1). A solution of *n*-butyllithium (1.6 M in hexane; 3.8 mL, 6 × 10^{-3} mol) was added dropwise to 1-methylpyrrole (0.8 mL, 9 × 10^{-3} mol) and TMEDA (0.9 mL, 6 × 10^{-3} mol) in 15 mL of dry THF at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 1 h. A solution of 1-cyano-3,4-dimethylphosphole[10] (0.82 g, 6 × 10^{-3} mol) in 5 mL of THF was added dropwise to the reaction mixture at room temperature. After evaporation of the solvent, the residue was chromatographed on alumina with toluene as the eluent: yield 0.75 g (65%).

^{31}P NMR (CD_2Cl_2): δ −32. ^{1}H NMR (CD_2Cl_2): δ 2.17 (dd, ^{4}J(H−P) = 3.8, ^{4}J(H−H) = 0.8, 6H, Me−C), 3.2 (s, 3H, Me−N), 6.21 (m, ^{3}J(H−H) = 3.3 and 2.4, ^{4}J(H−P) = 3.4, Hβ' pyrrole), 6.56 (dd, ^{2}J(H−P) = 37, ^{4}J(H−H) = 0.8, 2H, Hα phosphole), 6.69 (ddd, ^{4}J(H−H) = 1.7, ^{3}J(H−H) = 3.3, ^{3}J(H−P) = 5.1, Hβ pyrrole), 6.88 (dd, ^{3}J(H−H) = 2.4, ^{4}J(H−H) = 1.7, Hα' pyrrole). ^{13}C NMR (CD_2Cl_2): δ 18.3 (d, ^{3}J(C−P) = 3.9, Me−C), 34.05 (s, Me−N), 108.9 (d, ^{3}J(C−P) = 12.6, Cβ' pyrrole), 118.0 (d, ^{1}J(C−P) = 18.5, Cα pyrrole), 123.4 (d, ^{2}J(C−P) = 37.8, Cβ pyrrole), 129.0 (d, ^{1}J(C−P) = 13.2, Cα phosphole), 129.1 (s, Cα' pyrrole), 148.6 (d, ^{2}J(C−P) = 12, Cβ phosphole). MS of the dimeric oxide: *m/z* 414 (M^+, 26), 208 (M/2 + H, 100). Anal. Calcd for $C_{11}H_{14}NP$: C, 69.10; H, 7.38. Found: C, 69.41; H, 7.39.

1-(β-Cyanoethyl)-2-(1-methyl-2-pyrrolyl)-3,4-dimethylphosphole (3). A solution of phosphole **1** (0.76 g, 4 × 10^{-3} mol) in 20 mL of THF with ^{t}BuOK (0.56 g, 5 × 10^{-3} mol) was heated for 3 days at 160 °C to cleanly give the phospholide **2** (K^+) (δ^{31}P 74, ^{2}J(P−H) = 40). Then, $BrCH_2CH_2CN$ (0.42 mL, 5 × 10^{-3} mol) was added at room temperature to instantaneously give the phosphole **3**. After evaporation of the solvent, the residue was chromatographed on alumina with dichloromethane as the eluent: yield 0.64 g (65%). ^{31}P NMR (C_6D_6): δ −0.2. ^{1}H NMR (C_6D_6): δ 1.65 (m, 4H, P−CH_2CH_2CN), 1.92 (d, ^{4}J(H−P) = 3.4, 3H, Me−C_3), 2.02 (dd, ^{4}J(H−P) = 2.8, ^{4}J(H−H) = 1.4, 3H, Me−C_4), 3.28 (s, 3H, Me−N), 6.22 (dd, ^{4}J(H−H) = 1.8, ^{3}J(H−H) = 3.5, Hβ pyrrole), 6.25 (dq, ^{2}J(H−P) = 39, ^{4}J(H−H) = 1.4, Hα' phosphole), 6.44 (dd, ^{3}J(H−H) = 2.6 and 3.5, Hβ' pyrrole), 6.65 (dd, ^{4}J(H−H) = 1.8, ^{3}J(H−H) = 2.6, Hα' pyrrole). ^{13}C NMR (C_6D_6): δ 13.44 (d, ^{2}J(C−P) = 3.1, CH_2-CN), 15.87 (s, *Me*−C), 18.99 (d, ^{3}J(C−P) = 2.8, *Me*−C), 20.27 (d, ^{1}J(C−P) = 24.4, P−CH_2), 35.23 (d, ^{4}J(C−P) = 7.8, Me−N), 109.29 (s, Cβ' pyrrole), 110.97 (d, ^{3}J(C−P) = 4.5, Cβ pyrrole), 120.29 (d, ^{3}J(C−P) = 5.4, CN), 124.42 (s, Cα' pyrrole), 126.76 (d, ^{1}J(C−P) = 5.7, Cα' phosphole), 129.23 (Cα pyrrole, partly masked), 136.85 (d, ^{1}J(C−P) = 2.1, Cα phosphole), 146.32 (d, ^{2}J(C−P) = 12.5, Cβ phosphole), 153.00 (d, ^{2}J(C−P) = 4.5 Hz, Cβ' phosphole). MS: *m/z* 244 (M^+, 100), 204 (M − CH_2CN, 56), 190 (M − CH_2CH_2CN, 50). Anal. Calcd for $C_{14}H_{17}N_2P$: C, 68.84; H, 7.01. Found: C, 68.42; H, 7.01.

Bis(η^5-[2-(1-methyl-2-pyrrolyl)-3,4-dimethylphospholyl])iron (4). A solution of *n*-butyllithium (1.6 M in hexane; 1.25 mL, 2 × 10^{-3} mol) was added dropwise to phosphole **3** (0.44 g, 1.8 × 10^{-3} mol) in 10 mL of THF at −80 °C. The reaction mixture was warmed to room temperature and anhydrous $FeCl_2$ (0.11 g, 0.9 × 10^{-3} mol) was added. The mixture was heated at 45 °C for 30 min. After evaporation of the solvent, the residue was chromatographed on alumina with dichloromethane as the eluent. A mixture of meso and rac **4** was obtained: yield 0.09 g (23%). Further careful chromatography on alumina with CH_2Cl_2 provided a pure sample of the major meso isomer which was eluted first. Meso **4**. ^{31}P NMR (CD_2Cl_2): δ −55.7. ^{1}H NMR (CD_2Cl_2): δ 2.09 (s, 3H, Me−C), 2.18 (s, 3H, Me−C), 3.39 (s, 3H, Me−N), 3.83 (d, ^{2}J(H−P) = 36.1, CH−P), 5.97 (m, 2H, H$\beta\beta'$ pyrrole), 6.58 (m, 1H, Hα' pyrrole). ^{13}C NMR (CD_2Cl_2): δ 14.95 (s, *Me*−C), 16.71 (s, *Me*−C), 35.39 (d, ^{4}J(C−P) = 9.5, Me−N), 83.01 (d, ^{1}J(C−P) = 59.1, CH−P), 94.74 (d, ^{1}J(C−P) = 58.0, P−*C*-pyrrole), 95.32 (s, Cβ phosphole), 93.37 (d, Cβ phosphole), 107.15 (s, Cβ' pyrrole), 111.39 (s, Cβ pyrrole), 123.57 (s, Cα' pyrrole), 129.80 (m, Cα pyrrole). MS: *m/z* 436 (M^+, 100). Anal. Calcd for $C_{22}H_{26}FeN_2P_2$: C, 60.57; H, 6.01. Found: C, 60.43; H, 6.17.

1-(2-Bromophenyl)-3,4-dimethylphosphole (5). A mixture of lithium 3,4-dimethylphospholide (3.2 × 10^{-2} mol), prepared from lithium metal and 1-phenyl-3,4-dimethylphosphole,[10] 1,2-dibromobenzene (7.55 g, 3 × 10^{-2} mol), and anhydrous nickel bromide (0.35 g, 1.6 × 10^{-3} mol) in THF (100 mL) was heated to reflux for 4 h. After evaporation of the solvent, the residue was chromatographed on silica gel first with hexane and then hexane:toluene (80:20) giving **5** as a colorless oil (4.4 g, 54.9%). ^{31}P NMR ($CDCl_3$): δ 0.9. ^{1}H NMR ($CDCl_3$): δ 2.15 (dd, ^{4}J(H−P) = 3.7, ^{4}J(H−H) = 0.7, 6H, Me), 6.66 (dd, ^{2}J(H−P) = 37.3, ^{4}J(H−H) = 0.7, 2H, =CH), 7.09−7.26 (m, 3H), 7.53−7.59 (m, 1H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.90 (d, ^{3}J(C−P) = 3.7, Me), 126.90 (d, ^{1}J(C−P) = 2.3, =CH), 149.43 (d, ^{2}J(C−P) = 9.2, =C-), 127.40 (s, C_5 Ph), 129.02 (d, ^{2}J(C−P) = 27.3 Hz, C_2−Br Ph), 129.53 (s, C_4 Ph), 132.35 (s, C_3 Ph), 132.80 (d, ^{2}J(C−P) = 38.4, C_6 Ph), 136.65 (d, ^{1}J(C−P) = 10.8, C_1 Ph). MS: *m/z* (relative intensity), isotope pattern for M: calcd 266 (100), 267 (14), 268 (98), 269 (13); found 266 (100), 267 (20), 268 (98), 269 (15). Anal. Calcd for $C_{12}H_{12}BrP$: C, 53.96; H, 4.53; Br, 29.91; P, 11.60. Found: C, 54.02; H, 4.63; Br, 30.01; P, 11.46.

1-[2-(Diphenylphosphino)phenyl]-3,4-dimethylphosphole (7). A solution of bromophenylphosphole **5** (5.34 g, 2 × 10^{-2} mol) in THF (100 mL) was cooled to −60 °C. Butyllithium (1.5 M) in hexane (14.6 mL, 2.2 × 10^{-2} mol) was added, followed by chlorodiphenylphosphine after 15 min (4.85 g, 2.2 × 10^{-2} mol). The mixture was stirred for 0.5 h. After evaporation of THF, the residue was dissolved in a small quantity of CH_2Cl_2, deposited on silica gel, and chromatographed, first with hexane and then with hexane:CH_2Cl_2 (50:50). Phosphole **7** was obtained as a white solid: mp 138 °C, yield 4.8 g (65%). ^{31}P NMR (CH_2Cl_2): δP_A −7.0 (phosphole) and P_B −10.5 (PPh_2), $^{3}J(P_A−P_B)$ = 110. ^{1}H NMR ($CDCl_3$): δ 1.99 (d, ^{4}J(H−P) = 3.4, 6H, Me), 6.13 (ddd, $^{2}J(H−P_A)$ = 35.5, $^{5}J(H−P_B)$ = 1.6, ^{4}J(H−H) = 0.6, 2H, =CH), 6.91 (m, 1H), 7.08 (m, 3H, phenylene), 7.30 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.79 (d, ^{3}J(C−P) = 6.4, Me), 128.59 (d, ^{3}J(C−P) = 6.4, Ph *o*-C), 128.75 (s, Ph *p*-C), 129.02 (s, phenylene C_4 and C_5), 129.25 (d, ^{1}J(C−P) = 5.0, =CH), 132.49 (d, ^{3}J(C−P) = 5.9, C_3 or C_6), 133.19 (d, ^{3}J(C−P) = 7.8, C_6 or C_3), 134.13 (d, ^{2}J(C−P) = 18.6, Ph *o*-C), 137.07 (pseudo q, Ph ipso C), 138.72 (dd, ^{2}J(C−P) = 31.8, ^{1}J(C−P) = 7.6, C_1 or C_2), 143.30 (dd, ^{2}J(C−P) = 30.2, ^{1}J(C−P) = 7.0, C_2 or C_1), 148.65 (d, ^{2}J(C−P) = 8.8, =C−). MS: *m/z* (relative intensity): 372 (M, 100). Anal. Calcd for $C_{24}H_{22}P_2$: C, 77.41; H, 5.95; P, 16.64. Found: C, 77.31; H, 5.94; P, 16.41.

Potassium 2-[2-(Diphenylphosphino)phenyl]-3,4-dimethylphospholide (8). A solution of phosphole **7** (0.5 g, 1.3 × 10^{-3} mol) and potassium *tert*-butoxide (0.17 g, 1.56 × 10^{-3} mol) in THF (3 mL) was heated for 4 h at 150 °C in a pressure tube, leading to the phospholide ion **8**. ^{31}P NMR (THF): δ_A 86.2 (P^-), δ_X −14.7 (PPh_2), $^{4}J(P_A−P_X)$ = 25. ^{13}C NMR (THF): δ 15.52 (s, Me), 18.50 (s, Me), 148.96 (dd, $^{1}J(C−P_A)$ = 40.8, $^{3}J(C−P_X)$ = 9.0, Cα phospholide), 154.29 (dd, $^{2}J(C−P_X)$ = 33.2, $^{2}J(C−P_A)$ = 20.6, C ipso-C_6H_4). MS (negative ion, NH_3, 70 eV): *m/z* 371 (M^-, 35), 197 (100).

Bis[2-(2-(diphenylphosphino)phenyl)-3,4-dimethylphospholyl]palladium (9). To a solution of anion **8** (0.67 × 10^{-3} mol) in THF (4 mL) was added cyclooctadienepalladium dichloride (0.15 g, 0.4×10^{-3} mol). After evaporation of the solvent ($T \leq 30$ °C), the residue was dissolved in toluene and the solution filtrated on a short column of silica gel. The evaporation yielded **9** as a red microcrystalline solid: 0.1 g (33%). ^{31}P NMR (C_6D_6): δ_A 60.1 (P^-), δ_X 24.2 (PPh_2), $J(P_A-P_X) = 24.2$. MS m/z for ^{106}Pd (relative intensity): 848 (M, 25), 371 (M − Pd $^1/_2$, 100); isotope pattern for M^+ (relative intensity calcd; found) 846 (27.2; 30), 847 (68.9; 69.5), 848 (100.0; 100), 849 (44.7; 46.5), 850 (76.3; 76.5), 851 (37.3; 37), 852 (38.4; 37.5), 853 (17.3; 16), 856 (4.4; 4.5).

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