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Synthesis and Characterization of an Unsymmetrical 1, 2-Diphosphinoethanide Complex

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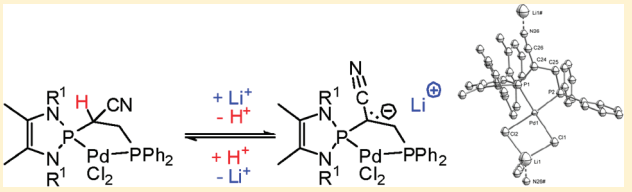
Supporting Information

ABSTRACT: A palladium 1,2-ethylene-bisphosphine complex prepared by diphosphination of acrylonitrile and subsequent complexation undergoes facile and reversible C deprotonation at a backbone carbon atom. The 1,2-diphosphinoethanide complex that formed was characterized by spectroscopic data and a single-crystal X-ray diffraction study. The reaction may explain the previously observed configurational lability of coordinated 1, 2-bisphosphine ligands with electron-withdrawing substituents.



Unsymmetrically substituted N-heterocyclic diphosphanes such as **1a,b** (Scheme 1) exhibit highly reactive P—P bonds that add under very mild conditions to electron-poor double or triple bonds to give the bidentate 1,2-bisphosphines **2** and **3**,[1] thus allowing the simultaneous introduction of two P-donor moieties with different electronic properties at an organic backbone.

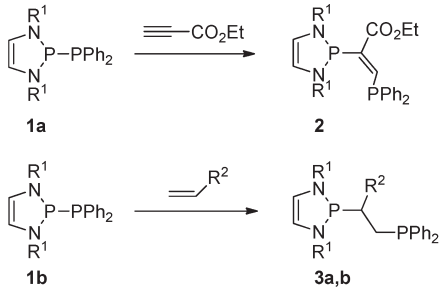
Whereas the diphosphination of alkynes is *Z* stereospecific[2−4] and yields a single stereoisomer, addition to alkenes produces racemic mixtures of enantiomers with *R* and *S* configurations at the newly formed stereogenic center at one of the backbone carbon atoms.[1,5] A particularly interesting case is provided by reactions of diphosphane **4** with 1,2-disubstituted alkenes (Scheme 2), where a pair of initially formed diastereomeric adducts with *meso* and *dl* configurations at the two backbone carbon atoms gave a single stereoisomer of complexes **5** and **6** after reaction with (cod)$PdCl_2$ (cod = 1,5-cyclooctadiene).[5] Although it had been suspected that this epimerization may be catalyzed by either Lewis bases or Lewis acids,[5] its actual mechanism remained unknown. Here, we report on a similar reaction sequence, involving N-heterocyclic diphosphane addition to acrylonitrile and complexation of formed 1,2-bisphosphine to palladium, which allowed for the isolation of a reaction intermediate that provides consistent proof for a base-catalyzed epimerization mechanism.

RESULTS AND DISCUSSION

The N-heterocyclic diphosphane **8** was prepared by analogy to the synthesis of **1a,b**[1] via metathesis of chlorodiazaphospholene **7** with lithium diphenylphosphide (Scheme 3).

The identity of **8** was established by spectroscopic data and a single-crystal X-ray diffraction study (Figure 1). The molecular structure of **8** is notable for showing a P—P bond even longer (P1—P2 = 2.347(1) Å vs a standard P—P distance in diphosphanes

Scheme 1



R^1 = 2,6-$Me_2C_6H_4$ (**1a, 2**), Mes (**1b, 3a,b**); R^2 = CN (**3a**), CO_2Me (**3b**)

of 2.221 ± 0.11 Å[6]) than those for **1b** (2.334(1) Å[1]), **4** (2.312 (1) Å[5]), or symmetrical bis-diazaphospholenes (2.24—2.33 Å[7]), which reflects the extra inductive stabilization of the diazaphospholenium cation fragment by the electron-releasing methyl groups.[8] The P—P bond lengthening had previously been identified as a typical feature of CC-unsaturated N-heterocyclic diphosphanes and is closely related to their high chemical reactivity.[9]

Reaction of diphosphane **8** with acrylonitrile at 50 °C produced the single addition product **9**, which was detected by ^{31}P NMR (AX spin system, δ 111.1 (PN_2), −16.0 (PPh_2), $^3J_{PP}$ = 12.3 Hz) and directly trapped by addition of (cod)$PdCl_2$ (Scheme 3). Complex **10** was isolated as a yellow powder; its purity and constitution were established by analytical and spectroscopic studies. The $^{31}P\{^1H\}$ NMR spectrum of **10** displays a characteristic AX-type pattern whose chemical shifts allow easy assignment of the PN_2 (δ 119.7, $^3J_{PP}$ = 20 Hz) and PPh_2 (δ 55.6, $^3J_{PP}$ = 20 Hz) moieties.

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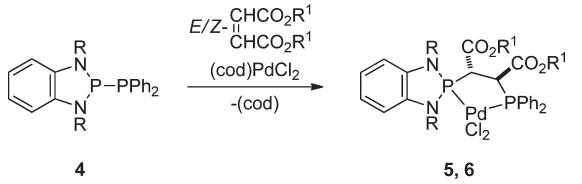
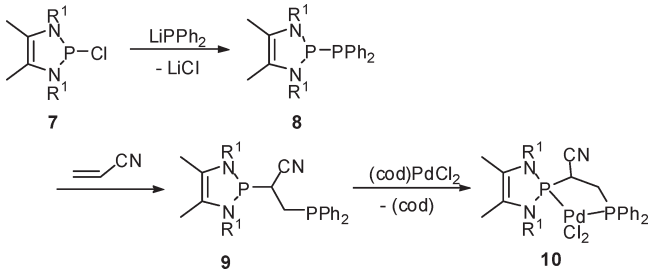
Scheme 2



R = $CH_2C(CH_3)_3$, R^1 = Et (**5**), Me (**6**)

Scheme 3[a]



[a] R^1 = 2,6-$Me_2C_6H_4$ (Dmp).

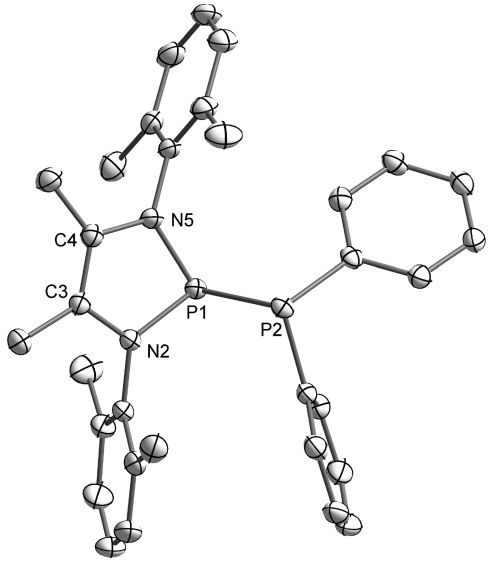
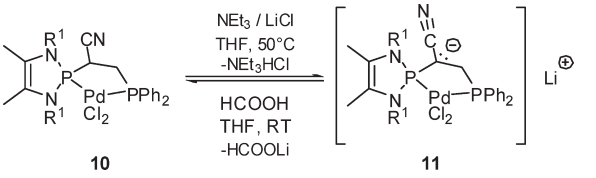


Figure 1. Molecular structure of **8** (H atoms omitted for clarity; displacement ellipsoids at the 50% probability level). Selected bond lengths (Å): P1−N2 = 1.705(1), P1−N5 = 1.706(1), P1−P2 = 2.347(1).

In order to study the possible influence of a base on the epimerization of the stereogenic center in the backbone of **10**, we performed the reaction of **7** with lithium diphenylphosphide, acrylonitrile, and (cod)$PdCl_2$ in a one-pot procedure in the presence of triethylamine. Instead of the expected complex **10**, we isolated in this case a product which was later identified as dimetallic complex **11**. The same product was also obtained from the reaction of pure complex **10** with appropriate amounts of triethylamine and lithium chloride (Scheme 4). The key step in this transformation is α-deprotonation of a doubly activated methylene group to give a

Scheme 4[a]



[a] R^1 = Dmp.

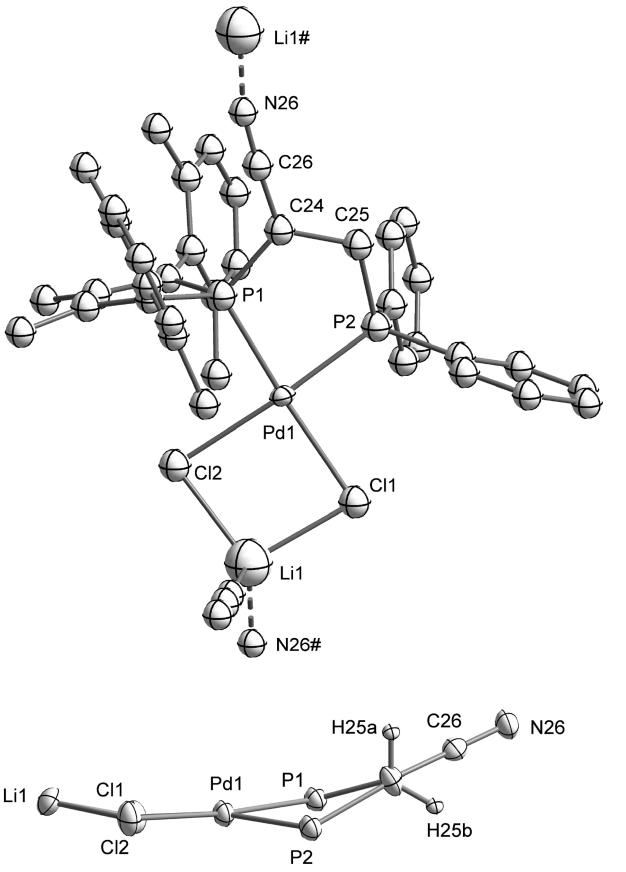


Figure 2. Representation of one formula unit of **11** in the crystal (top) and reduced plot without P substituents (bottom). H atoms and solvent molecules are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Li1# and N26# denote atoms of adjacent units in the coordination polymer generated by the symmetry operations $-1+x, y, z$ and $1+x, y, z$, respectively. Selected distances (in Å): Li1#−N26 = 1.971(11), Pd1−P1 = 2.242(1), Pd1−P2 = 2.219(1), Pd1−Cl1 = 2.427(1), Pd1−Cl2 = 2.431(1), P1−N2 = 1.697(5), P1−N5 = 1.706(5), P1−C24 = 1.716(5), C24−C25 = 1.514(8), C25−P2 = 1.814(5), C24−C26 = 1.407(7), C26−N26 = 1.147(6), Cl1−Li1 = 2.322(10), Cl2−Li1 = 2.334(10).

nitrile-stabilized carbanion. Species of this type are useful intermediates in organic synthesis.[10] α-Phosphanyl anions are less abundant but have also been prepared.[11]

Complex **11** was isolated after crystallization from acetonitrile. A single-crystal X-ray diffraction study revealed the presence of chloride-bridged dinuclear lithium−palladium complexes that are connected via interaction of the nitrile lone pair with the lithium ion of an adjacent formula unit to form a one-dimensional coordination polymer (Figure 2). Each lithium ion is

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further solvated by an additional acetonitrile molecule. The C24−C25 bond (1.514(8) Å) forming the backbone of the bisphosphine ligand is a normal single bond, whereas the C24−C26 distance (1.407(7) Å) is markedly shortened, indicating some electron delocalization between the formal carbanion center and the adjacent nitrile group. The C26−N26 distance (1.147(6) Å) and the N26−Li1 contact of 1.971(11) Å are typical for coordinated CN triple bonds.[12] The chelate bite angle (P1−Pd1−P2 = 84.80(5)°) is smaller than those in **5** and **6**,[4] related complexes of ethylene-1,2-bisphosphines such as **2**,[5] or similar specimens recently reported by Pringle et al.[2] (P−Pd−P = 88−90°). The PdP_2C_2 chelate ring displays a twist conformation, and the palladium coordination sphere shows a similar deviation from planarity as had been observed for **5** and **6**,[5] with a dihedral angle of 9° between the P1−Pd−P2 and Cl1−Pd−Cl2 planes. As a consequence of the μ_2-bridging chloride coordination, the Pd−Cl distances (Pd1−Cl1 = 2.427(1) Å, Pd1−Cl2 = 2.431(1) Å) are longer than those to the terminal chlorides in **5** and **6** (Pd−P = 2.35−2.37 Å[5]).

The molecular structure of **11** was further confirmed by ^{31}P solid-state NMR data. The ^{31}P CP/MAS NMR spectrum consists of two signals with chemical shifts of 108 and 55 ppm that are connected by a mutual coupling of 28 Hz, which was derived from a *J*-resolved 2D spectrum. Attempts to characterize **11** by ^{31}P solution NMR in THF produced spectra with several sets of signals, some of which showed substantial exchange broadening. Although no further signal assignment was attempted, these spectra indicate that the complex undergoes some reaction in solution.

In order to ascertain that complex **11** may be considered a genuine intermediate in the epimerization of the stereogenic center in **10**, it is essential to prove also the feasibility of the reverse reaction: i.e. reprotonation of **11** to give **10**. To this end, we reacted the THF solution of **11** with an excess of formic acid and established by monitoring the reaction by ^{31}P NMR that the neutral complex **10** was indeed formed as the only detectable product (Scheme 4).

CONCLUSIONS

In summary, we have demonstrated the facile and fully reversible interconversion between the neutral 1,2-bisphosphine complex **10** and its C-deprotonation product, **11**. The reaction allows a mechanistic explanation of the previously observed[5] backbone epimerization in the diphosphination of maleic esters. It appears plausible that the epimerization may be catalyzed by other bases (such as phosphines) and that anion formation is facilitated by the accumulation of electron-withdrawing nitrile and phosphenium substituents. In this respect, the results are not in contradiction with the configurational stability of certain ethane-1,2-bisphosphines such as Prophos, Chiraphos, Norphos,[13] and others, which lack any electron-withdrawing substituents, but suggest that other bisphosphines obtained by diphosphination of electron-poor alkenes may also be liable to a similar isomerization. Even though this behavior precludes using such species to control enantioselectivity in a catalytic process, it offers opportunities to develop novel "non-innocent" ligands for cooperative catalysis.[14]

EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of dry argon using standard vacuum line techniques. Solvents were dried by standard procedures. NMR spectra were recorded on Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.5 MHz; ^{31}P, 161.9 MHz) and Avance 250 (^{1}H, 250.1 MHz; ^{13}C, 62.8 MHz; ^{31}P, 101.2 MHz) NMR spectrometers at 303 K; chemical shifts are referenced to external TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (Ξ = 40.480 747 MHz, ^{31}P). Coupling constants are given as absolute values. Elemental analyses were determined on a Perkin-Elmer 24000CHN/O analyzer. Melting points were determined in sealed capillaries.

1,3-Bis(2′,6′-dimethylphenyl)-4,5-dimethyl-2-diphenylphosphino[1.3.2]diazaphospholene (8). A solution of *n*-BuLi (2.5 M in THF, 1.5 mL, 2.7 mmol) was added dropwise to a cooled (−78 °C) solution of diphenylphosphine (0.45 mL, 2.7 mmol) in THF (10 mL). After 15 min, the mixture was warmed to room temperature and stirred for 1 h. This solution was then slowly added to a cooled (−78 °C) solution of chloro-1,3-diazaphospholene **7**[15] (0.95 g, 2.7 mmol). Stirring was continued for 1 h after the addition was completed, and the solution was evaporated under reduced pressure. The residue was extracted with hexane (20 mL). The filtrate was filtered over Celite and concentrated to 5 mL. The product crystallized at 4 °C (yield 78%): mp 105 °C; ^{31}P NMR (C_6D_6) δ 147.4 (d, $^3J_{PP}$ = 288 Hz, N_2P), −24.9 (d, $^3J_{PP}$ = 288 Hz, PPh_2). Anal. Calcd for $C_{32}H_{34}N_2P_2$ (508.57): C, 75.57; H, 6.74; N, 5.51. Found: C, 74.62; H, 6.71; N, 5.52.

2-[1,3-Bis(2′,6′-dimethylphenyl)[1.3.2]diazaphospholenyl]-3-(diphenylphosphino)propanenitrile (9) and Its Dichloropalladium Complex (10). Acrylonitrile (0.14 mL, 2.1 mmol) was added to a stirred solution of **8** (0.75 g, 2.1 mmol) in THF (15 mL), and the mixture was stirred for 4 h at 50 °C. ^{31}P NMR spectroscopy revealed the formation of **9** (δ 111.1 (d, $^3J_{PP}$ = 12.3 Hz, N_2P), −16.0 (d, $^3J_{PP}$ = 12.3 Hz, PPh_2)) together with minor amounts of species resulting from hydrolysis of **8**.[4] A solution of (cod)$PdCl_2$ (0.29 g, 1.05 mmol) in CH_2Cl_2 (15 mL) was then slowly added. The solution was stirred for a further 0.5 h after the addition was completed and evaporated under reduced pressure. The residue was extracted with diethyl ether (20 mL) and filtered. The solvent was evaporated to leave an orange powder (yield 38%): mp 174 °C; ^{31}P NMR (C_6D_6) δ 120.6 (d, $^3J_{PP}$ = 22 Hz, N_2P), 59.2 (d, $^3J_{PP}$ = 22 Hz, PPh_2); ^{1}H NMR (C_6D_6) δ 7.44−7.28 (m, 10 H, H_{phenyl}), 7.18−7.04 (m, 6 H, H_{phenyl}), 3.24−3.09 (m, 1 H, CN−CH), 2.98 (s, 3 H, *o*-CH_3), 2.82 (s, 3 H, *o*-CH_3), 2.45 (s, 3 H, *o*-CH_3), 2.38(s, 3 H, o-CH_3), 2.18−2.09 (m, 1 H, CH_2), 2.02−1.95 (m, 1 H, CH_2), 1.69 (d, 6 H, $^4J_{PH}$ = 4.75 Hz, N−CH_3); ^{13}C{^{1}H}NMR (C_6D_6) δ 138.4 (d, $^1J_{PC}$ = 62.3 Hz, *i*-C_{phenyl}), 138.3 (d, $^1J_{PC}$ = 62.1 Hz, *i*-C_{phenyl}), 136.0 (d, $^2J_{PC}$ = 50.5 Hz, *i*-C_{Dmp}), 135.9 (d, $^2J_{PC}$ = 50.1 Hz, *i*-C_{Dmp}), 132.3 (d, $^5J_{PC}$ = 4.2 Hz, *p*-C_{phenyl}), 132.0 (d, $^5J_{PC}$ = 11.9 Hz, *o*-C_{phenyl}), 131.8 (d, $^5J_{PC}$ = 4.9 Hz, *p*-C_{phenyl}), 131.7 (d, $^5J_{PC}$ = 11.5 Hz, *o*-C_{phenyl}), 130.6 (d, $^3J_{PC}$ = 3.1 Hz, *o*-C_{Dmp}), 128.6 (s, broad, *o*-C_{Dmp}), 127.5 (d, $^5J_{PC}$ = 0.9 Hz, *p*-C_{Dmp}), 127.4 (s, broad, *m*-C_{phenyl}), 127.3 (s, *m*-C_{Dmp}), 127.2 (s, *m*-C_{Dmp}), 127.1 (s, broad, *m*-C_{phenyl}), 126.9 (d, $^5J_{PC}$ = 1.3 Hz, *p*-C_{Dmp}), 123.8 (d, $^2J_{PC}$ = 5.2 Hz, N−CCH_3), 123.0 (d, $^2J_{PC}$ = 5.2 Hz, N−CCH_3), 38.2 (dd, $^2J_{PC}$ = 5.6 Hz, $^1J_{PC}$ = 41.1 Hz, CN−CH), 25.3 (dd, $^2J_{PC}$ = 21.2 Hz, $^1J_{PC}$ = 30.2 Hz, CH_2), 21.7 (d, $^4J_{PC}$ = 1.0 Hz, *o*-CH_3), 21.1 (s, broad, *o*-CH_3), 17.9 (d, $^4J_{PC}$ = 0.6 Hz, *o*-CH_3), 17.8 (s, broad, *o*-CH_3), 9.5 (d, $^3J_{PC}$ = 3.3 Hz, N−CH_3), 9.4 (d, $^3J_{PC}$ = 3.3 Hz, N−CH_3); IR $\tilde{\nu}$(CN) 2236 (w) cm^{-1}. Anal. Calcd for $C_{35}H_{37}Cl_2N_3P_2Pd$ (738.96): C, 56.89; H, 5.05; N, 5.69. Found: C, 56.47; H, 5.26; N, 5.00.

Deprotonation of 10 To Give 11. Palladium complex **10** (0.2 g, 0.27 mmol), 2 equiv of triethylamine, and 1 equiv of LiCl were dissolved in anhydrous THF (10 mL) and stirred for 3 h at 50 °C. The solution was cooled to room temperature and evaporated under reduced pressure. The residue was dissolved in acetonitrile (5 mL) and stored at 4 °C to yield red crystals (yield 83%): dec pt 172 °C; ^{31}P CP/MAS NMR δ 108 (N_2P), 55 (Ph_2P), $^3J_{PP}$ = 28 Hz. Anal. Calcd for $C_{35}H_{37}Cl_2N_3P_2PdLi$ (744.89): C, 56.43; H, 4.87; N, 5.64. Found: C, 56.48; H, 4.88; N, 6.18.

Protonation of 11. Complex **11** (120 mg) and 1 drop of formic acid were dissolved in d_8-THF (1 mL) and stirred for 15 min. Quantitative protonation to give **10** was confirmed by ^{31}P NMR spectroscopy. No attempt at isolation of the product was made.

^{31}P NMR (THF-d_8): δ 119.7 (d, $^3J_{PP}$ = 22 Hz, N_2P), 55.6 (d, $^3J_{PP}$ = 22 Hz, PPh_2).

Crystallography. Crystal structure determinations of **8** and **11** were performed on a Nonius KappaCCD diffractometer at T = 123(2) K using Mo Kα radiation (λ = 0.710 73 Å). Direct methods (SHELXS-97)[16] were used for structure solution, refinement was carried out using SHELXL-97[16] (full-matrix least-squares on F^2), and hydrogen atoms were refined using a riding model. A semiempirical absorption correction was applied for **11**. Data for **8**: orange crystals, $C_{32}H_{34}N_4P_2$, M_r = 508.55, crystal size 0.35 × 0.30 × 0.25 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 8.051(2) Å, b = 12.213(3) Å, c = 14.472(1) Å, α = 84.28(2)°, β = 80.99(2)°, γ = 78.72(2)°, V = 1374.8(5) Å^3, Z = 2, ρ = 1.229 Mg m^{-3}, μ(Mo Kα) = 0.182 mm^{-1}, T = 123(2) K, F(000) = 540, $2\theta_{max}$ = 55°, 30 636 reflections, 6280 of which were independent (R_{int} = 0.031), 331 parameters, R1 = 0.037 (for $I > 2\sigma(I)$), wR2 = 0.093 (all data), S = 1.03, largest difference peak/hole 0.340/−0.236 e Å^{-3}. Data for **11**: red crystals, $C_{37}H_{39}Cl_2LiN_4P_2Pd \cdot 2CH_3CN$, M_r = 868.01, crystal size 0.40 × 0.20 × 0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 10.471(1) Å, b = 14.436(1) Å, c = 15.933(2) Å, α = 107.57(1)°, β = 102.66(1)°, γ = 109.74(1)°, V = 2018.0(3) Å^3, Z = 2, ρ = 1.429 Mg m^{-3}, μ(Mo Kα) = 0.709 mm^{-1}, T = 123(2) K, F(000) = 892, $2\theta_{max}$ = 55°, 22 821 reflections, 9125 of which were independent (R_{int} = 0.077), 487 parameters, R1 = 0.070 (for $I > 2\sigma(I)$), wR2 = 0.191 (all data), S = 1.02, largest difference peak/hole 1.616/−0.926 e Å^{-3}.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving X-ray structural information on **8** (CCDC-807699) and **11** (CCDC-807700). This material is available free of charge via the Internet at http://pubs.acs.org.

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