ORGANIC LETTERS

2009
Vol. 11, No. 15
3338−3341

Phosphole-Triazole Hybrids: A Facile Synthesis and Complexation with Pd(II) and Pt(II) Salts

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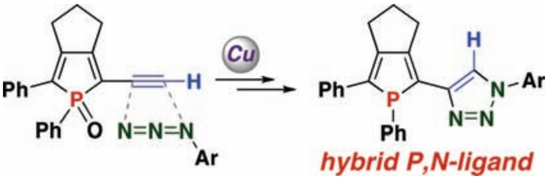
Received May 28, 2009

ABSTRACT



The copper-promoted Huisgen reaction of α-ethynylphosphole *P*-oxides with aryl azides affords α-(1-aryl-1,2,3-triazol-4-yl)phospholes in high yield. The α-(1-phenyl-1,2,3-triazol-4-yl)phosphole exhibits different coordination behavior in the complexation with MCl_2(cod) (M = Pd, Pt). It has been revealed that P,N-coordination to $PdCl_2$ dramatically changes the optical properties of the newly constructed phosphole-triazole hybrid π-system.

Phospholes bearing *N*-heteroaryl substituents exhibit characteristic optical and coordinating properties endowed by the P and N atoms.[1] The synergetic effects of these two heteroatoms are of particular interest to the application of such ligands to the fields of materials, supramolecular, and synthetic chemistry. For example, Réau and co-workers have demonstrated that the NLO property of α-(2-pyridyl)phospholes and the chiroptical property of phosphole-modified aza[6] helicenes were remarkably enhanced by P,N-chelation with a cationic palladium salt.[1c,k] In addition, palladium and ruthenium complexes bearing phosphole-containing P,N-heteroditopic ligands have shown high catalytic activities in olefin/CO copolymerization,[1b] transfer hydrogenation of ketones,[1d] and cross-coupling reactions.[1e,f] Despite these promising results, however, the number of N-heteroaryl substituents examined is quite limited. In this context, it is of significance to develop a reliable methodology for introducing a series of *N*-heteroaryl groups onto the phosphole ring, as well as to reveal the optical, electrochemical, and coordinating properties of the resulting phosphole-based hybrid π-systems.

Quite recently, we have established a convenient method for the synthesis of silyl-capped 2-ethynylphosphole **1** and 2,5-diethynylphosphole **2** (Figure 1).[2] Notably, **1** and **2** were readily converted to the acetylene-linked phosphole-arene

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[1] For example, see: (a) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulászi, L.; Réau, R. *Chem.—Eur. J.* **2001**, *7*, 4222–4236. (b) Sauthier, M.; Leca, F.; Toupet, L.; Réau, R. *Organometallics* **2002**, *21*, 1591–1602. (c) Fave, C.; Hissler, M.; Sénéchal, K.; Ledoux, I.; Zyss, J.; Réau, R. *Chem. Commun.* **2002**, 1674–1675. (d) Thoumazet, C.; Melaimi, M.; Ricard, L.; Mathey, F.; Le Floch, P. *Organometallics* **2003**, *22*, 1580–1581. (e) Melaimi, M.; Thoumazet, C.; Ricard, L.; Le Floch, P. *J. Organomet. Chem.* **2004**, *689*, 2988–2994. (f) Thoumazet, C.; Melaimi, M.; Ricard, L.; Le Floch, P. *C. R. Chimie* **2004**, *7*, 823–832. (g) Welsch, S.; Lescop, C.; Scheer, M.; Réau, R. *Inorg. Chem.* **2008**, *47*, 8592–8594. (h) Matano, Y.; Miyajima, T.; Ochi, N.; Nakabuchi, T.; Shiro, M.; Nakao, Y.; Sakaki, S.; Imahori, H. *J. Am. Chem. Soc.* **2008**, *130*, 990–1002. (i) Matano, Y.; Nakabuchi, T.; Fujishige, S.; Nakano, H.; Imahori, H. *J. Am. Chem. Soc.* **2008**, *130*, 16446–16447. (j) Nohra, B.; Rodriguez-Sanz, E.; Lescop, C.; Réau, R. *Chem.—Eur. J.* **2008**, *14*, 3391–3403. (k) Graule, S.; Rudolph, M.; Vanthuyne, N.; Autschbach, J.; Roussel, C.; Crassous, J.; Réau, R. *J. Am. Chem. Soc.* **2009**, *131*, 3183–3185. (l) Crassous, J.; Réau, R. *Dalton Trans. (Perspective)* **2009**, 6865–6876, and references therein.

10.1021/ol901194m CCC: $40.75

π-systems by using cross- and homocoupling methods. We anticipated that the acetylene functions in **1** and **2** would also be applicable to Huisgen-type [2 + 3] cycloaddition reactions[3] affording the corresponding five-membered heterocycles. Here we report the first facile synthesis of α-(1-aryl-1,2,3-triazol-4-yl)phospholes from **1**/**2** and aryl azides. As we expected, the dipolar cycloaddition proceeded efficiently with the assistance of a copper salt. The substituent and complexation effects on the optical properties of the newly developed phosphole-triazole-arene π-systems are also reported.

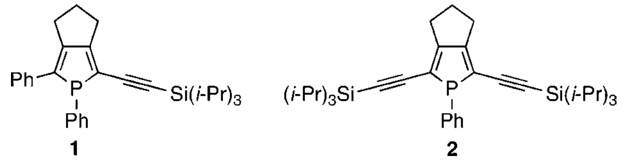
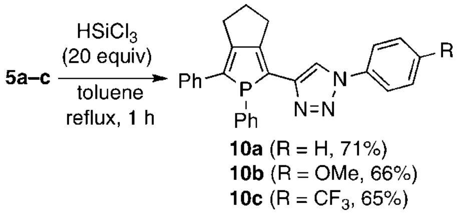


Figure 1. Silyl-capped 2-ethynylphosphole **1** and 2,5-diethynylphosphole **2**.

The starting materials, silyl-capped α-ethynylphospholes **1** and **2**, were prepared according to the reported procedure.[2] Treatment of **1** with tetra-*n*-butylammonium fluoride (TBAF) in THF followed by addition of *m*-chloroperbenzoic acid (*m*CPBA) generated α-ethynylphosphole *P*-oxide **3** [δ_P = 52.8 ppm; δ_H (acetylene) = 3.46 ppm (d, J = 3.9 Hz); m/z = 316.1017 (M$^+$)] in high NMR yield (Scheme 1). As **3** slowly decomposed in solution, the crude product was subsequently treated with aryl azides **4a**−**c** in the presence of $CuSO_4{\cdot}5H_2O$ and sodium ascorbate. As expected, the Huisgen dipolar cycloaddition occurred efficiently to give the corresponding 2-(1-aryl-1,2,3-triazol-4-yl)phospholes **5a**−**c** in 81−86% yields based on **1**.[4] Similarly, 2,5-bis(1-aryl-1,2,3-triazol-4-yl)phospholes **7a**−**c** were prepared in 74−77% yields from **2** via terminal-free phosphole *P*-oxide **6** [δ_P = 51.0 ppm; δ_H (acetylene) = 3.49 ppm (d, J = 3.9 Hz); m/z = 264.0704 (M$^+$)]. When 2,7-diazido-9,9-dihexylfluorene (**8**) was used as the N_3 source, fluorene-bridged phosphole-triazole hybrid **9** was isolated in 86% yield. Overall, the Huisgen reaction has proven to be applicable to the synthesis of phosphole derivatives bearing triazole substituents at the α positions.

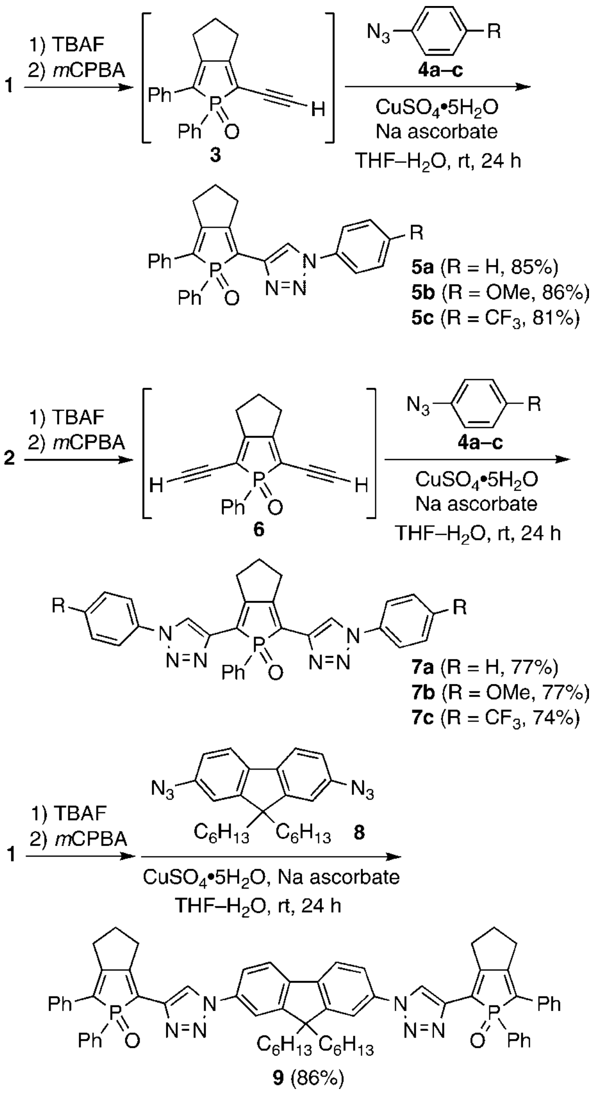
Deoxygenation of **5a**−**c** with trichlorosilane proceeded in refluxing toluene to give the respective σ^3-P type compounds **10a**−**c** in 65−71% yields (eq 1).



(1)

Compounds **5**, **7**, **9**, and **10** were fully characterized by conventional spectroscopic techniques. There is little difference in ^{31}P chemical shifts among **5a**, **5b**, and **5c**, implying that the electronic effects of the *para*-substituents on the phosphorus nuclei are negligible (Table 1). The same is true for **7a**−**c** and **10a**−**c**.

Scheme 1. Synthesis of **5**, **7**, and **9**



The crystal structure of **7a** was further elucidated by X-ray crystallography.[5] As shown in Figure 2, one triazole ring (N1−N3−C8) is somewhat twisted as compared to the other

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[2] Matano, Y.; Nakashima, M.; Imahori, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 4002–4005.

[3] (a) Huisgen, R. *Proc. Chem. Soc.* **1961**, 357. (b) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; pp 1−176.

[4] The phosphorus center was masked with the oxo group to prevent undesirable Staudinger reaction.

[5] **7a**: $C_{29}H_{23}N_6OP$, triclinic, $P\bar{1}$, a = 8.7372(15), b = 9.6953(16), c = 16.196(3) Å, α = 73.121(8)°, β = 82.282(11)°, γ = 64.087(7)°, V = 1180.8(4) Å^3, Z = 2, ρ_{calcd} = 1.413 g cm^{-3}, collected 9212, independent 5248, parameters 335, R_w = 0.0865, R = 0.0412 ($I > 2.00\sigma(I)$), GOF = 1.067. **11**: $C_{27}H_{22}Cl_2N_3PPd{\cdot}2(C_2H_2Cl_4)$, triclinic, $P\bar{1}$, a = 8.1743(11), b = 13.1609(19), c = 17.591(3) Å, α = 80.241(4)°, β = 76.545(4)°, γ = 84.462(5)°, V = 1810.7(4) Å^3, Z = 2, ρ_{calcd} = 1.710 g cm^{-3}, collected 21770, independent 7954, parameters 416, R_w = 0.0850, R = 0.0389 ($I > 2.00\sigma(I)$), GOF = 1.086.

Table 1. ^{31}P NMR Chemical Shifts, UV−vis Absorption and Fluorescence Maxima, and Redox Potentials of **5**, **7**, **9**, and **10**

compd	δ_P/ppm^a	λ_{abs}/nm (log ε)^b	λ_{em}/nm (Φ_f)^{b,c}	E_{ox}/V^{d,e}	E_{red}/V^{d,e}
5a	53.4	386 (4.18)	489 (0.03)	+1.02	−2.04
5b	53.4	388 (4.19)	492 (0.02)	+0.97	−2.05
5c	53.3	384 (4.19)	486 (0.03)	+1.07	−2.02
7a	52.6	390 (4.20)	492 (0.04)	+1.03	−1.99
7b	52.6	393 (4.21)	495 (0.03)	+0.97	−2.01
7c	52.4	388 (4.23)	486 (0.03)	+1.11	−1.95
9	53.3	389 (4.61)	490 (0.03)	n.d.	n.d.
10a	31.8	370 (4.28)	448 (0.09)	n.d.	n.d.
10b	31.7	371 (4.29)	451 (0.14)	n.d.	n.d.
10c	32.7	372 (4.29)	448 (0.11)	n.d.	n.d.

[a] Measured in $CDCl_3$, vs H_3PO_4. [b] Measured in THF. [c] $\lambda_{ex} = 365$ nm. Fluorescence quantum yield relative to that of Réau's 3,4-C_4-bridged 1-phenyl-2,5-bis(2-thienyl)phosphole ($\Phi_f = 0.050$). [d] Measured in CH_2Cl_2, vs Fc/Fc$^+$. Reference electrode Ag/Ag$^+$ [0.01 M $AgNO_3$, 0.1 M n-Bu_4NPF_6 (MeCN)]. [e] n.d. = not determined.

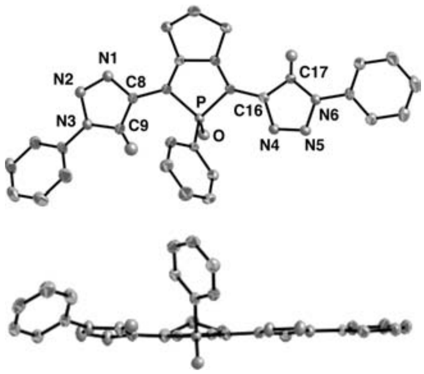
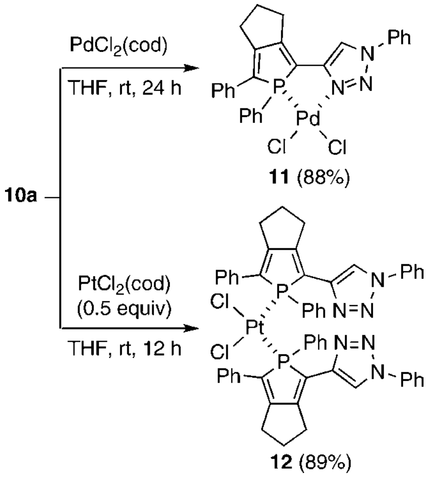


Figure 2. Top (upper) and side (lower) views of **7a**. Hydrogen atoms (except for triazole-CH) are omitted for clarity. Selected bond lengths (Å): N1−N2 = 1.312(2), N2−N3 = 1.356(2), N4−N5 = 1.306(2), N5−N6 = 1.3578(19).

(N4−N6−C16). The twisted conformation may be caused by the steric repulsion between the P-substituents and the *syn*-oriented triazole-CH group. The N1−N2 and N4−N5 bond lengths are shorter by ca. 0.04−0.05 Å than the N2−N3 and N5−N6 bond lengths, representing that the double bond character of the former bonds is larger than that of the latter.

To reveal the π-conjugation efficiency of the phosphole-triazole-benzene hybrids, the absorption and fluorescence spectra of **5a**−**c**, **7a**−**c**, and **10a**−**c** were compared (Table 1 and Figure S1 in Supporting Information). The P-oxidation causes bathochromic shifts of λ_{abs} and λ_{em} values ($\Delta\lambda_{abs}$ = 12−17 nm and $\Delta\lambda_{em}$ = 38−41 nm for **5a**−**c** vs **10a**−**c**) as observed for typical phosphole-based π-systems.[1] Among **5a**−**c**, there are very small differences in λ_{abs} and λ_{em} values ($\Delta\lambda_{max} \leq 6$ nm). The same is true for **7a**−**c** ($\Delta\lambda_{max} \leq 9$ nm) and **10a**−**c** ($\Delta\lambda_{max} \leq 3$ nm), indicating that the electronic effects of *para*-substituents on the phosphole-triazole-arene hybrid π-systems are not so significant. Indeed, there are slight differences in redox potentials among **5a**−**c** (ΔE = 0.03−0.10 V) and **7a**−**c** (ΔE = 0.06−0.14 V). These are in sharp contrast to the results observed for the phosphole-acetylene-arene[2] and phosphole-vinylene-arene[6] hybrid π-systems. To get more insight into the π-conjugation structures, we performed density functional theory (DFT) calculations on model compounds of **7a**−**c**. As shown in Figure S2 in Supporting Information, HOMO and LUMO of **7am**, **7bm**, and **7cm** consist of those originated mainly from the phosphole-triazole subunits, and the contribution of the N-aryl rings is little. This reasonably explains the experimentally observed, small *para*-substituent effects.

Scheme 2. Complexation of **10a** with MCl_2(cod) (M = Pd, Pt)



With new phosphole-containing P,N-ligands in hand, we examined the complexation with Pd(II) and Pt(II) salts (Scheme 2). Compound **10a** reacted with $PdCl_2$(cod) (cod = 1,5-cyclooctadiene) in THF at room temperature to give Pd-complex **11** in 88% yield. Spectroscopic and X-ray crystallographic analyses (vide infra) have elucidated that the phosphole-triazole subunit in **11** coordinates to the palladium(II) center as the P,N-bidentate ligand. On the other hand, **10a** underwent complexation with a half amount of $PtCl_2$(cod) to yield $PtCl_2$-bisphosphine complex **12** as a sole product. The formation of **12** was exclusive even when an equimolar amount of the Pt source was employed. The ^{31}P resonance of **11** appeared at δ 80.0, whereas that of **12** appeared at δ 34.0 with Pt−P satellites. The ^{195}Pt−^{31}P coupling constant of 3287 Hz indicates *cis* orientation of the two phosphine ligands in **12**. The ^{1}H NMR peaks of the triazole-methine protons of **11** and **12** were observed at δ 8.05 and 8.78, respectively, which also reflects their different coordination modes.

Figure 3 depicts the crystal structure of **11**.[5] The palladium center adopts a square planar geometry with the phosphorus and nitrogen atoms at *cis* orientation. Due to the P,N-chelation, the phosphole and triazole rings are twisted significantly as observed for palladium complexes bearing heteroditopic α-(2-pyridyl)phosphole ligands.[1b,f,7] The Pd−P and Pd−N bond lengths of **11** [2.2401(8) and 2.055(2) Å]

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(6) Matano, Y.; Miyajima, T.; Imahori, H.; Kimura, Y. *J. Org. Chem.* **2007**, *72*, 6200–6205.

are comparable to those of Réau's $PdCl_2$-α-(2-pyridyl)phosphole complex [2.2353(11) and 2.076(4) Å].[7] The Pd−Cl1 bond length [2.2768(8) Å] is appreciably shorter than the Pd−Cl2 bond length [2.3429(8) Å], which is attributable to a difference in *trans* influence between the P and N donors. Although the refined data are not at the publishable level, the *cis* coordination of two phosphole rings in **12** was confirmed by X-ray crystallography.

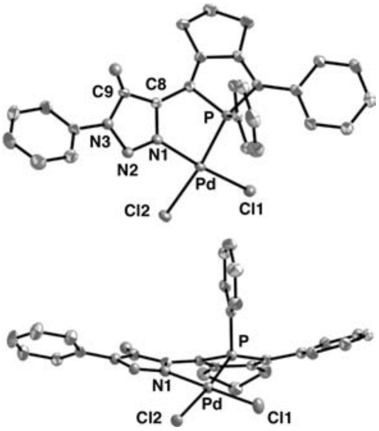

Figure 3. Top and side views of **11**. Hydrogen atoms (except for triazole-CH) and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−P, 2.2401(8); Pd−N1, 2.055(2); Pd−Cl1, 2.2768(8); Pd−Cl2, 2.3429(8); N1−N2, 1.302(3); N2−N3, 1.337(3); P−Pd−N1, 80.63(7); P−Pd−Cl1, 94.77(3); N1−Pd−Cl2, 91.82(7); Cl1−Pd−Cl2, 92.69(3).

To reveal the effect of metal coordination on the electronic structure of the phosphole-triazole π-system, we measured absorption spectra of **10a**, **11**, and **12** in 1,1,2,2-tetrachloroethane (Figure 4). The absorption maximum of platinum-bisphosphine complex **12** is red-shifted as compared to that of **10a** without a significant change in the spectral shape, implying that the Pt-complexation basically affects the energy levels of the frontier orbitals. On the other hand, the palladium chelate complex **11** displays a completely different, broad spectrum with relatively low extinction coefficients at the visible region. This may be attributable to charge-transfer as well as orbital interactions between the metal and the π-ligand and also to the twisted π-conjugated system of **11**. As a whole, the chelation-induced modulation of π−π* transitions of the phosphole-triazole π-system is achieved by adding a Pd(II) salt.

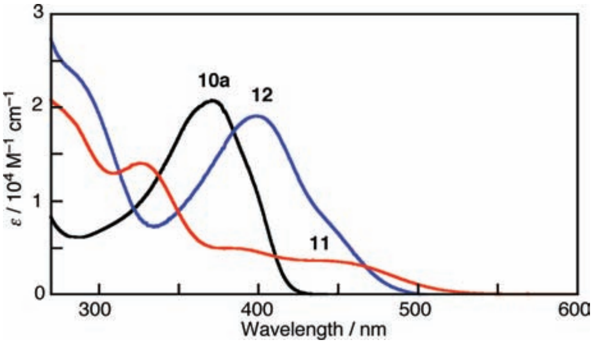

Figure 4. UV−vis absorption spectra of **10a** (black), **11** (red), and **12** (blue) in $Cl_2CHCHCl_2$.

In summary, we have explored a conceptually new method for the synthesis of phospholes bearing *N*-heterocyclic substituents, which relies on Huisgen dipolar [2 + 3] cycloaddition reactions. Using this method, α-(1-aryl-1,2,3-triazol-4-yl)phospholes were readily accessible from the corresponding α-ethynylphospholes and aryl azides through the assistance of the copper promoter. Although the electronic effects of the *para*-substituents of the terminal benzene rings are small, the metal complexation as well as the oxidation at the phosphorus center has proven to perturb the optical properties of the phosphole-triazole π-conjugated system. In particular, the *cis*-P,N-chelation to the Pd(II) center has a significant impact on the electronic structure of this hybrid π-system. The present results feature a new aspect of π-conjugated phosphole-containing heteroditopic ligands, which may be applicable to the construction of unique metal-assisted supramolecular π-networks.

Acknowledgment. This work was partially supported by the Asahi Glass Foundation.

Supporting Information Available: Experimental details, DFT computational results, ^1H NMR spectra, and CIF files for **7a** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[7] Leca, F.; Lescop, C.; Toupet, L.; Réau, R. *Organometallics* **2004**, *23*, 6191–6201.