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Article

Unprecedented Ring Transformation of an α,α′-Monosubstituted 2,4,5-Triphenylpyrylium Salt with η^3-Phosphines: Efficient Synthesis of Aryl- and Alkylphosphonium Triphenylcyclopentadienylides

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The ring transformation of the α-reactive 2,4,5-triphenylpyrylium salt **1** with η^3-phosphines to the aryl- and alkylphosphonium triphenylcyclopentadienylides **5** is reported. The mechanism of this unprecedented transformation might involve tandem conjugate addition and intramolecular Wittig cyclization.

Phosphonium cyclopentadienylide (PCPY) ligands have attracted increasing attention recently, owing to their potential applications in organometallic chemistry and catalytic fields.[1] However, the difficulties in the synthetic method and in characterization have induced very few PCPYs except for $C_5H_4PPh_3$, thus limiting the study of their chemistry to some extent. For example, the reactivities of most of these compounds remain largely unexplored and the effects of ligand substitution on metal complex structures and reactivities have been very little examined. On the other hand, it is proposed that the metal coordinating and subsequent catalytic behavior of the PCPY ligands could be partially dependent on the substituents on phosphorus.[2] As a result, the development of a novel synthetic route to PCPY ligands with different substituents on phosphorus is significant and necessary.

Ring transformation of pyrylium salts with various nucleophiles to synthesize a wide range of cyclic as well as heterocyclic compounds is of currently great interest to organic chemists. Up to now, various functional compounds starting from pyrylium salts have been prepared which are utilized in many fields, such as biology,[3] pharmaceutics,[4] nonlinear materials,[5] polymer science,[6] etc. Surprisingly, ring transformation of α-active (i.e., α.α′-nonsubstituted and monosubstituted) pyrylium salts has been much less investigated. In fact, owing to the "naked" positive charge at the α-position, such pyrylium salts should have much higher reactivity than their α-nonreactive counterparts.[7]

In our previous work, we reported an efficient synthetic method for pyrylium salts, especially for α-reactive pyrylium salts, by aerobic oxidation of polysubstituted cyclopentadienes.[8] Encouraged by this discovery, we investigate herein the reaction of the α-reactive 2,4,5-triphenylpyrylium salt **1** with nucleophilic η^3-phosphines. As a result, an unprecedented ring transformation of **1** to new PCPY ligands with different substituents on phosphorus was discovered. The corresponding results of our investigation are reported in this paper.

Experimental Section

All syntheses were carried out under a dry, deoxygenated argon atmosphere using standard Schlenk line techniques. NMR spectra were recorded on a Varian INOVA-400 spectrometer. Mass spectra were recorded on a HP 1100 MS spectrometer. Elemental analyses were carried out on a Shimadzu 6800 instrument.

All solvents used in this work such as CH_2Cl_2, CH_3CN, ethanol, toluene, and hexane were purified by the methods descried by Perrin et al.[9] All deuterated solvents were purchased

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from Cambridge Isotope Laboratories. Most chemicals were obtained from Aldrich and were used as received.

X-ray crystal structure determinations were performed on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using the SMART and SAINT programs. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1. All non-hydrogen atoms were refined anisotropically.

Trimethyl(2,3,5-triphenyl-1,3-pentadien-5-one)phosphonium Perchlorate (3a). A solution of 2,4,5-triphenylpyrylium perchlorate (**1**; 0.3 g, 0.735 mmol) in 20 mL of CH_3CN was treated dropwise with 0.056 g of PMe_3 (0.750 mmol) in 0.5 mL of toluene. The reaction mixture was stirred at room temperature for 1 h under an Ar atmosphere. When TLC showed the complete consumption of **1**, the solvent was removed in vacuo to yield an organic solid. Recrystallization from a mixture of CH_2Cl_2 and hexane gave product **3a** (0.310 g, 87%) as light yellow crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 8.07−7.38 (m, 16H), 6.64 (d, 1H, $^2J_{H-P}$ = 16.4 Hz), 1.73 (d, 9H, $^2J_{H-P}$ = 14.4 Hz). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 10.2, 108.1, 124.4, 127.4, 128.1, 128.7, 129.1, 129.7, 131.1, 131.5, 133.9, 136.7, 137.3, 137.5, 137.8, 149.3, 162.2, 189.2. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 15.4. MS (API-ES): m/z 385.1 (M^+). Anal. Calcd for ($C_{26}H_{26}OP^+$)(ClO_4^-): C, 64.46; H, 5.37; P, 6.40. Found: C, 64.53; H, 5.34; P, 6.36.

Triethyl(2,3,5-triphenyl-1,3-pentadien-5-one)phosphonium Perchlorate (3b). A procedure analogous to that for **3a** gave **3b** (0.351 g, 89%) as yellow crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.36−8.03 (m, 16H), 6.50 (d, 1H, $^2J_{H-P}$ = 14.0 Hz), 2.11−1.82 (m, 6H), 1.05−0.96 (m, 9H). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 5.9, 14.1, 103.4, 118.3, 125.0, 128.4, 129.0, 129.5, 129.9, 130.5, 132.0, 134.7, 138.2, 138.7, 138.9, 150.9, 166.6, 189.8. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 31.8. MS (API-ES): m/z 427.5 (M^+). Anal. Calcd for ($C_{29}H_{32}OP^+$)(ClO_4^-): C, 66.03; H, 5.10; P, 4.94. Found: C, 65.97; H, 5.06; P, 4.91.

Dimethylphenyl(2,3,5-triphenyl-1,3-pentadien-5-one)phosphonium Perchlorate (3c). A procedure analogous to that for **3a** gave **3c** (0.352 g, 86%) as yellow crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 6.80−7.84 (m, 21H), 5.93 (d, 1H, $^2J_{H-P}$ = 21.6 Hz), 1.67 (t, 6H, $^2J_{H-P}$ = 12.8 Hz). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 11.6, 106.3, 107.2, 118.2, 124.3, 128.3, 128.9, 129.3, 129.5, 129.7, 130.0, 130.1, 130.4, 130.7, 132.1, 134.5, 137.2, 1385, 139.0, 144.0, 150.2, 165.4, 189.4. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 14.1. MS (API-ES): m/z 447.5 (M^+). Anal. Calcd for ($C_{31}H_{28}OP^+$)(ClO_4^-): C, 68.01; H, 5.12; P, 5.67. Found: C, 67.89; H, 5.02; P, 5.66.

Diphenylmethyl(2,3,5-triphenyl-1,3-pentadien-5-one)phosphonium Perchlorate (3d). A procedure analogous to that for **3a** gave **3d** (0.351 g, 77%) as yellow crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.04−7.84 (m, 26H), 6.25 (d, 1H, $^2J_{H-P}$ = 22.0 Hz), 1.10 (t, 3H, $^2J_{H-P}$ = 7.2 Hz). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 10.6, 105.6, 118.3, 121.1, 124.3, 128.3, 128.6, 129.0, 129.6, 130.2, 130.5, 130.8, 132.9, 133.5, 133.7, 133.9, 134.5, 135.5, 135.6, 137.0, 138.4, 138.6, 139.4, 149.9, 167.1, 189.6. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 13.6. MS (API-ES): m/z 509.6 (M^+). Anal. Calcd for ($C_{36}H_{30}OP^+$)(ClO_4^-): C, 70.94; H, 4.93; P, 5.09. Found: C, 70.91; H, 4.91; P, 5.08.

Trimethyl(2,3,5-triphenylcyclopentadienyl)phosphonium Perchlorate (4a). A solution of 2,4,5-triphenylpyrylium perchlorate (**1**; 0.3 g, 0.735 mmol) in 20 mL of CH_3CN was treated dropwise with 0.112 g of PMe_3 (1.500 mmol) in 1 mL of toluene. The reaction mixture was refluxed for 6 h under an Ar atmosphere. When TLC monitoring showed the complete consumption of **1**, the solvent was removed in vacuo to yield an pale solid. Recrystallization from a mixture of CH_2Cl_2 and hexane gave product **4a** (0.29 g, 85%) as gray crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.16−7.69 (m, 16H), 5.81 (d, 1H, $^2J_{H-P}$ = 18.8 Hz), 1.30 (d, 9H, $^2J_{H-P}$ = 14.0 Hz). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 7.6, 55.7, 79.3, 128.9, 129.5, 129.6, 129.9, 130.3, 130.5, 130.6, 130.7, 130.8, 132.6, 135.5, 135.9, 136.5, 136.7, 144.1. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 31.26. MS (API-ES): m/z 369.1(M^+). Anal. Calcd for ($C_{26}H_{26}P^+$)(ClO_4^-): C, 66.67; H, 5.56; P, 6.62. Found: C, 66.77; H, 5.53; P, 6.55.

Triethyl(2,3,5-triphenylcyclopentadienyl)phosphonium Perchlorate (4b). A procedure analogous to that for **4a** gave **4b** (0.312 g, 83%) as gray crystals. ^{1}H NMR (acetonitrile-d_3, 0.400 MHz): δ 7.13−7.66 (m, 16H), 5.75 (d, 1H, $^2J_{H-P}$ = 20.8 Hz), 1.51−1.94 (m, 6H), 1.03 (m, 9H). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 6.5, 12.2, 49.1, 48.7, 128.5, 129.3, 129.5, 129.8, 130.2, 130.6, 131.0, 133.7, 135.4, 135.8, 137.5, 138.9, 139.5, 144.8, 147.7. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 42.67. MS (API-ES): m/z 411.3 (M^+). Anal. Calcd for ($C_{29}H_{32}P^+$)(ClO_4^-): C, 68.24; H, 6.27; P, 6.08. Found: C, 68.43; H, 6.26; P, 6.07.

Dimethylphenyl(2,3,5-triphenylcyclopentadienyl)-phosphonium Perchlorate (4c). A procedure analogous to that for **4a** gave **4c** (0.318 g, 82%) as gray crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 6.99−7.66 (m, 21H), 5.97 (d, 1H, $^2J_{H-P}$ = 22.0 Hz), 1.67 (t, 6H, $^2J_{H-P}$ = 13.6 Hz). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 7.7, 51.5, 51.9, 128.3, 129.1, 129.4, 129.5, 129.7, 129.9, 130.0, 130.4, 130.6, 132.6, 132.7, 134.6, 134.9, 135.5, 136.9, 137.0, 138.9, 143.8, 147.4. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 28.92. MS (API-ES): m/z 431.1 (M^+). Anal. Calcd for ($C_{31}H_{28}P^+$)-(ClO_4^-): C, 70.19; H, 5.28; P, 5.85. Found: C, 70.01; H, 5.29; P, 5.83.

Diphenylmethyl(2,3,5-triphenylcyclopentadienyl) phosphonium Perchlorate (4d). A procedure analogous to that for **4a** gave **4d** (0.344 g, 79%) as gray crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 6.86−8.42 (m, 26H), 6.33 (d, 1H, $^2J_{H-P}$ = 22.0 Hz), 1.12 (t, 3H, $^2J_{H-P}$ = 7.2 Hz). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 5.9, 52.1, 116.6, 118.3, 128.3, 128.4, 128.9, 129.1, 129.4, 129.7, 129.9 130.3, 130.4, 130.5, 130.9, 131.0, 132.8, 133.5, 134.5, 134.7, 135.3, 135.5, 136.3, 139.2, 143.6, 147.3. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 23.8. MS (API-ES): m/z 493.2 (M^+). Anal. Calcd for ($C_{36}H_{30}P^+$)(ClO_4^-): C, 70.19; H, 5.28; P, 5.85. Found: C, 70.01; H, 5.29; P, 5.83.

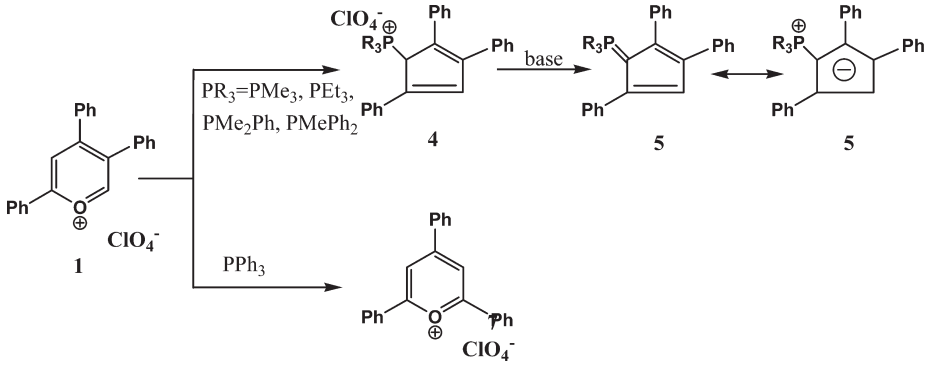
Trimethylphosphonium 2,3,5-Triphenylcyclopentadienylide (5a). A suspension of **4a** (0.468 g, 0.001 mol) in ethanol (20 mL) was added to an aqueous solution of NaOH (2 N, 2 mL). The mixture was stirred for 10 min and then left for 6 h at room temperature. The deep red precipitate was filtered off and recrystallized from acetonitrile to give the ylide **5a** (0.323 g, 88%). ^{1}H NMR (chloroform-d, 400 MHz): δ 6.91−7.49 (m, 15H), 6.41 (d, 1H, $^4J_{H-P}$ = 6.4 Hz), 1.37 (d, 9H, $^2J_{H-P}$ = 13.2 Hz). ^{13}C NMR (chloroform-d, 100 MHz): δ 16.5, 82.7, 83.9, 116.0, 123.2, 125.3, 125.9, 126.9, 127.0, 127.4, 128.0, 129.6, 129.9, 131.6, 132.8, 139.8, 141.5, 141.9. ^{31}P NMR (chloroform-d, 100 MHz): δ 2.87. Anal. Calcd for $C_{26}H_{25}P$: C, 84.78; H, 6.79; P, 8.43. Found: C, 84.72; H, 6.83; P, 8.45.

Triethylphosphonium 2,3,5-Triphenylcyclopentadienylide (5b). A procedure analogous to that for **5a** gave **5b** (0.365 g, 89%). ^{1}H NMR (chloroform-d, 400 MHz): δ 6.89−7.82 (m, 15H), 6.56 (d, 1H, $^4J_{H-P}$ = 6.8 Hz), 1.92 (m, 6H), 1.43 (d, 9H, $^2J_{H-P}$ = 13.2 Hz). ^{13}C NMR (chloroform-d, 100 MHz): δ 14.9, 79.0, 80.0, 116.7, 123,2, 125.0, 125.7, 127.4, 127.5, 129.5, 130.8, 131.0, 131.9, 132.3, 133.7, 133.8, 139.9, 141.1, 141.6. ^{31}P NMR (chloroform-d, 100 MHz): δ 4.83. Anal. Calcd for $C_{29}H_{31}P$: C, 84.88; H, 7.56; P, 7.56. Found: C, 84.84; H, 7.57; P, 7.59.

Dimethylphenylphosphonium 2,3,5-Triphenylcyclopentadienylide (5c). A procedure analogous to that for **5a** gave **5c** (0.353 g, 82%). ^{1}H NMR (chloroform-d, 400 MHz): δ 6.89−7.80 (m, 20H), 6.56 (d, 1H, $^4J_{H-P}$ = 6.8 Hz), 1.40 (d, 6H, $^2J_{H-P}$ = 13.2 Hz). ^{13}C NMR (chloroform-d, 100 MHz): δ 14.9, 79.0, 80.0, 116.6, 123.2, 125.0, 125.7, 127.6, 127.9, 128.0, 129.3, 129.5, 130.9, 131.0, 131.1, 131.7, 131.9, 132.3, 133.8, 139.9, 141.2, 141.6. ^{31}P NMR (chloroform-d, 100 MHz): δ 4.88. Anal. Calcd for $C_{31}H_{27}P$: C, 86.51; H, 6.28; P, 7.21. Found: C, 86.47; H, 6.30; P, 7.23.

Diphenylmethylphosphonium 2,3,5-Triphenylcyclopentadienylide (5d). A procedure analogous to that for **5a** gave **5d** (0.395 g, 80%). ^{1}H NMR (chloroform-d, 400 MHz): δ 6.84−7.54 (m, 25H),

Scheme 1. Ring Transformation of 1 with Various Nucleophilic η^3-Phosphines



6.60 (d, 1H, $^4J_{H-P}$ = 6.4 Hz), 1.66 (d, 3H, $^2J_{H-P}$ = 12.8 Hz). ^{13}C NMR (chloroform-*d*, 100 MHz): δ 31.0, 79.4, 116.9, 123.2, 124.4, 125.2, 127.5, 127.7, 127.9, 128.1, 128.4, 128.9, 129.6, 130.6, 130.7, 131.7, 131.9, 132.2, 132.9, 134.8, 140.0, 141.3. ^{31}P NMR (chloroform-*d*, 100 MHz): δ 9.04. Anal. Calcd for $C_{36}H_{29}P$: C, 87.63; H, 5.88; P, 6.49. Found: C, 87.58; H, 5.90; P, 6.52.

Trimethyl(1,3,5-triphenyl-4-trimethylphosphoranylidene-2-en-5-one)phosphornium Perchlorate (8). A procedure analogous to that for the synthesis of compounds **4** gave **8** (0.21 g, 51%) as gray crystals. ^{1}H NMR (acetonitrile-d_3, 400 MHz): δ 7.44−7.85 (m, 16H), 1.81 (d, 1H, $^2J_{H-P}$ = 13.6 Hz), 1.58 (d, 9H, $^2J_{H-P}$ = 14.0 Hz), 1.34 (d, 9H, $^2J_{H-P}$ = 14.0 Hz). ^{13}C NMR (acetonitrile-d_3, 100 MHz): δ 5.8, 11.2, 28.5, 28.7, 28.9, 29.1, 29.3, 41.4, 41.7, 54.2, 122.4, 127.5, 128.4, 128.7, 129.5, 129.8, 129.9, 130.4, 141.5. ^{31}P NMR (acetonitrile-d_3, 100 MHz): δ 32.61, 13.46. MS (API-ES): m/z 461.1 (M^+). Anal. Calcd for ($C_{29}H_{35}OP_2^+$)(ClO_4^-): C, 62.03; H, 6.24; P, 11.05. Found: C, 62.09; H, 6.19; P, 11.04.

Results and Discussion

The pyrylium salt **1** was synthesized on the basis of our previously reported work.[8] The key distinguishing structural feature of **1** is that there is no substituent at the 6-position of the pyrylium ring, which causes it to be more easily attacked by nucleophiles. In this case, we tried the reaction of **1** with nucleophilic η^3-phosphines with the aim of obtaining some new phosphorus-containing functional compounds. As shown in Scheme 1, the ring transformation of **1** exhibited two different pathways, depending on the properties of the η^3-phosphines used.

When PPh_3 was chosen as the nucleophilic agent to react with **1**, the corresponding 2,4,6-triphenyl pyrylium salt **7** was obtained as the sole product. A comparison of the resonance structures of 2,4,5- and 2,4,6-triphenylpyrylium cations shows that the presence of a phenyl group at the 6-position makes cation **7** more stable than cation **1**. Accordingly, it is thought that PPh_3 herein might act as the catalyst to rearrange the 2,4,5-triphenylpyrylium salt **1** to the more stable 2,4,6-triphenylpyrylium salt **7**. The details of this conversion need further investigation.

Significantly, when **1** was reacted with PMe_3, PEt_3, PMe_2Ph, and $PMePh_2$, which are relatively less sterically demanding compared to PPh_3, the ring contraction products, the triphenylcyclopentadienyl phosphonium salts **4**, were obtained in good yields. The structures of **4** were fully characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, MS, and elemental analyses. Luckily, a single crystal of **4a** suitable for X-ray diffraction determination could be grown by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **4a** (Figure 1).

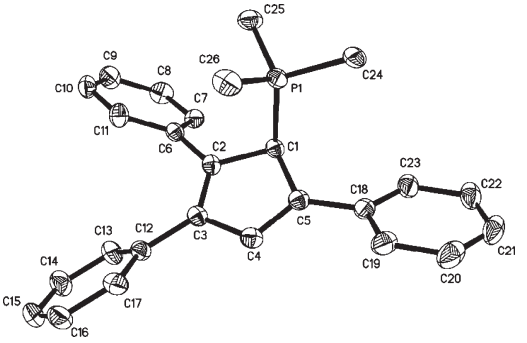
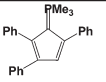
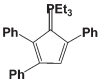
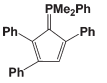
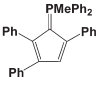


Figure 1. Crystal structure of compound **4a**. The anion has been omitted for clarity.

Table 1. Access to PCPY Ligands 5 from Ring Contraction of 1

Entry	*Nucleophiles*	*Time [h]*	*product*		*Yield[a] [%]*
1	PMe_3	6		5a	75
2	PEt_3	6		5b	74
3	PMe_2Ph	8		5c	67
4	$PMePh_2$	10		5d	63

[a] Isolated yields.

Treatment of compounds **4** with sodium hydroxide gives the target PCPY ligands **5** in excellent yields.[11] The synthetic results are summarized in Table 1.

It is clear that the ring contraction of pyrylium salt **1** reported herein provides a novel synthetic route to PCPY ligands, especially PCPY ligands with different substituents on phosphorus, which are useful in exploring the effects of ligand substitution on metal complex structures and reactivities. In order to know more details about the reaction process,

(10) (a) Brownie, J. H.; Baird, M. C. *J. Organomet. Chem.* **2008**, *693*, 2812. (b) Brownie, J. H.; Baird, M. C.; Laws, D. R.; Geiger, W. E. *Organometallics* **2007**, *26*, 5890. (c) Brownie, J. H.; Baird, M. C.; Schmider, H. *Organometallics* **2007**, *26*, 1433. (d) Brownie, J. H.; Baird, M. C.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2003**, *22*, 33.

(11) Lloyd, D.; Singer, M. I. C. *J. Chem. Soc. C* **1971**, 2941.

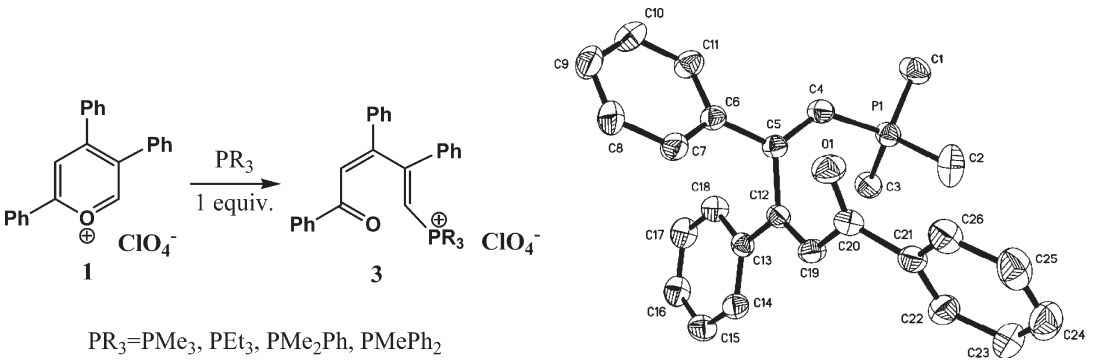
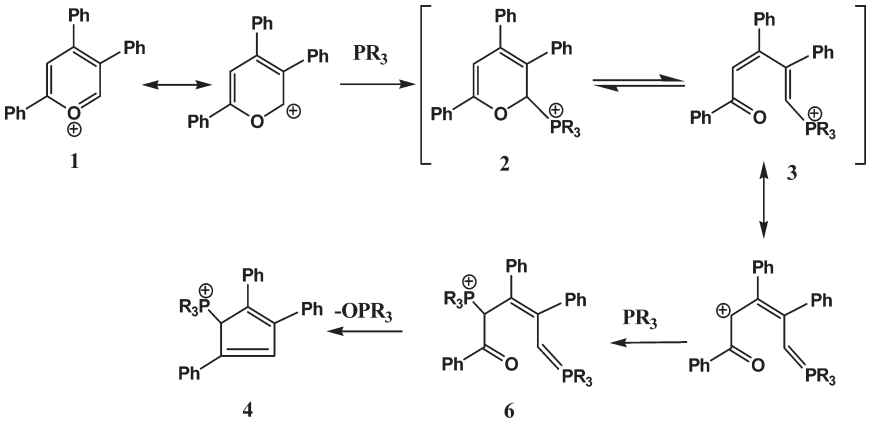


Figure 2. Reaction of **1** with equimolar PR_3 (left) and the crystal structure of compound **3a** (right). The anion has been omitted for clarity.

Scheme 2. Proposed Mechanism for Ring Transformation from Pyrylium Salt 1 to Cyclopentadienyl Phosphonium Salt 4



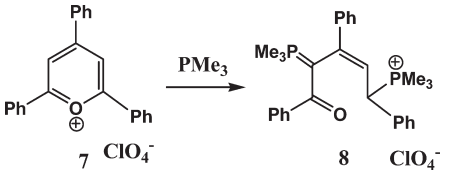
further investigation was done accordingly. It was found that not only the structural properties but also the amount of phosphines used could affect the formation of final products. For example, use of over 2 equiv of η^3-phosphines could completely convert **1** to the ring-contraction product **4**. In contrast, the reaction of an equimolar amount of η^3-phosphines with **1** yielded only the ring-opening product **3**. An X-ray-quality single crystal of **3a** was also obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution of **3a** (Figure 2).

Further work showed significantly that the reaction of compound **3** with additional η^3-phosphines gave solely the cyclopentadienylphosphonium salts **4**. This result clearly indicated that compound **3** was the key intermediate of the transformation from pyrylium salt **1** to cyclopentadienylphosphonium salts **4**. In this case, a plausible mechanism for this transformation is proposed (Scheme 2).

At the first step, due to the more concentrated positive charge at the α-position, attack by the first equivalent of PR_3 should occur at this position to give the 2*H*-pyran **2**, which readily undergoes ring opening to its more stable valence tautomer **3**. This process is accordance with the well-known ring-opening reaction of a general pyrylium ring induced by nucleophilic agents.[12] The subsequent conjugated addition to **3** by another equivalent of phosphine gives the acyclic phosphorus ylide **6**, which undergoes an intramolecular Wittig reaction to a cyclopentadiene ring, producing the final product, the cyclopentadienyl phosphonium salt **4**. Our attempts to isolate compound **6** were unsuccessful, due to its rapid conversion to compound **4**.

(12) Markl, G.; Lieb, F.; Merz, A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 944.

Scheme 3. Reaction of 2,4,6-Triphenylpyrylium Salt 7 with 2 Equiv of PMe_3



To confirm the effect of α-reactivity of pyrylium salt **1** on this novel ring transformation, we investigated the reaction of the 2,4,6-triphenylpyrylium salt **7** with PMe_3. As expected, no ring contraction to a cyclopentadienyl phosphonium salt was observed. Instead, the acyclic compound **8** was obtained as the sole product (Scheme 3). Accordingly, it is apparent that the steric hindrance of the phenyl group at the 6-position inhibits the intramolecular Wittig reaction. This result indicates the important role of α-reactivity of the pyrylium cation and provides further evidence for the proposed mechanism shown in Scheme 2.

In comparison with the well-documented $C_5H_4PPh_3$ ligand, the coordination properties of PCPY ligands with other substituents on phosphorus and the C_5H_4 ring have been less investigated. In this regard, ring transformation of the pyrylium salt **1** to new PCPY ligands provides the chance to do further research in this field. Luckily, we obtained crystals of **5c**, and on the basis of this crystal structure, its electronic structure has been primarily investigated using DFT methodologies (Figure 3). The calculated results demonstrate that the almost degenerate HOMO orbitals have symmetries rather similar to those of the corresponding

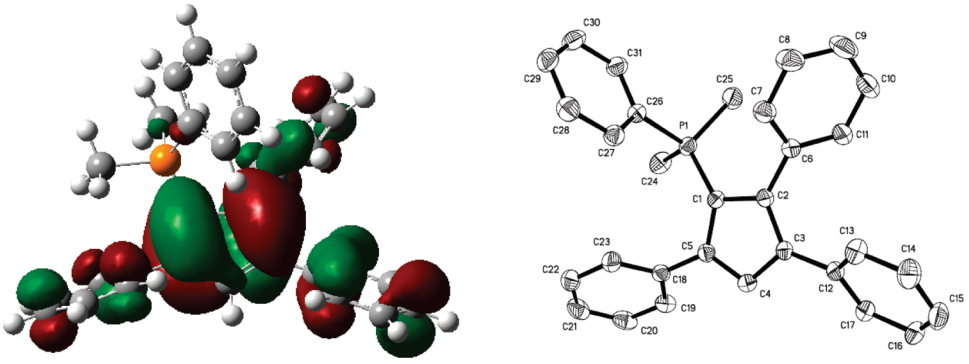


Figure 3. Contour plot of the HOMO of **5c** (left; contour values are ±0.05) and the X-ray crystal structure of **5c** (right).

HOMO (doubly degenerate; E1 symmetry) of the cyclopentadienyl anion. This is consistent with the electronic structure implied by resonance for $C_5H_4PPh_3$ and $C_5H_4PMePh_2$ which has been reported.[1,10] The coordination properties of these new aryl- and alkylphosphonium cyclopentadienylides **5** toward various transition metals are still being conducted in our laboratory.

Summary

In summary, we have reported an unprecedented ring contraction of the α-reactive 2,4,5-triphenylpyrylium salt **1** with η^3-phosphines and its utility in the efficient synthesis of new PCPY ligands **5**. The preliminary results supported the plausible mechanism of a tandem conjugate addition and intramolecular Wittig reaction, during which the α-reactivity of pyrylium salt **1** has a profound effect on this ring contraction. Those findings are valuable in terms of the design and synthesis of new PCPY ligands with different substituents and the exploitation of their coordination chemistry with various metal ions.

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Supporting Information Available: Figures, tables, and CIF files giving all spectra for synthesized compounds and single-crystal data for **3a**, **4a**, and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.