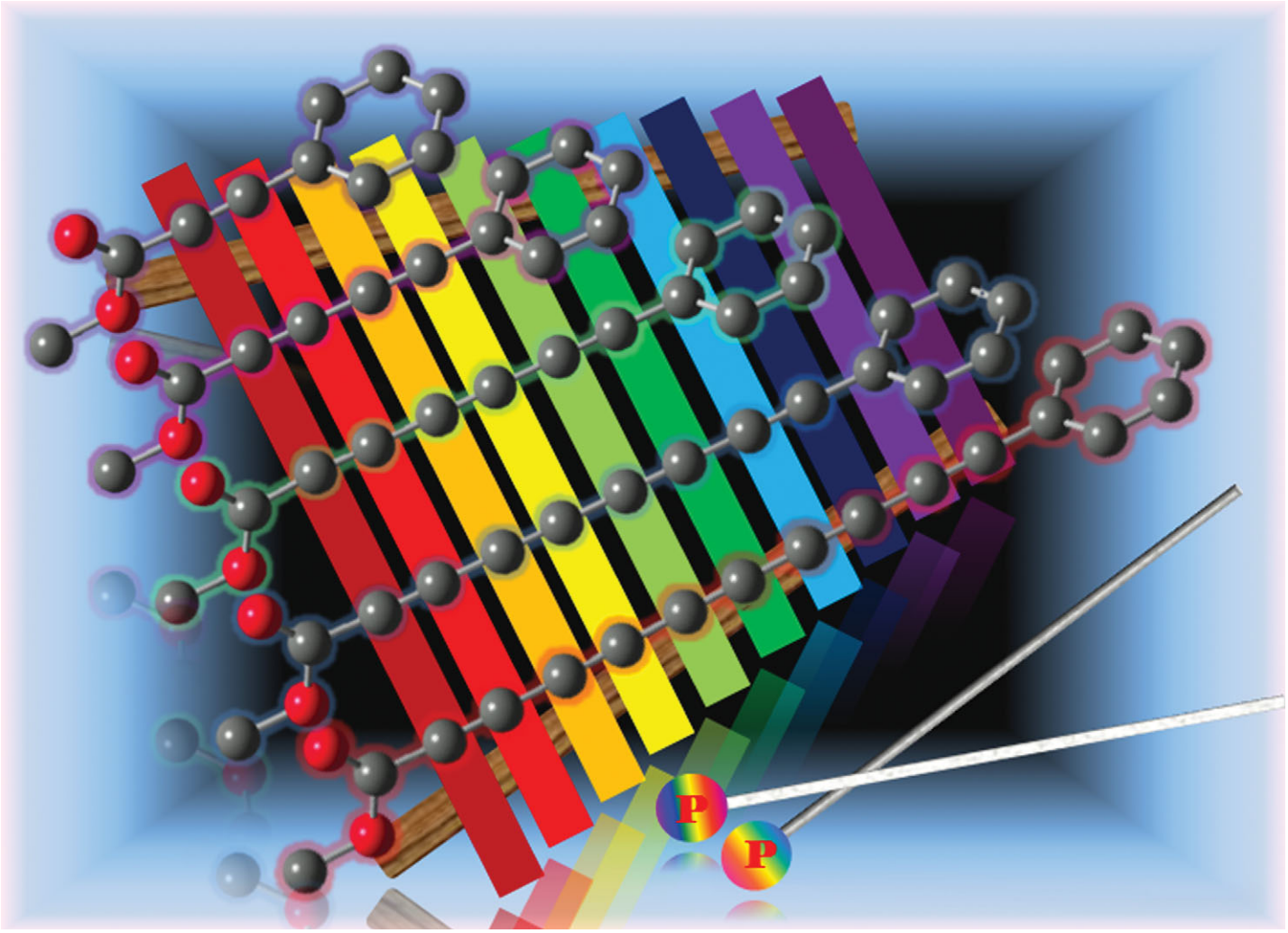


Featuring research of Jie-Cheng Deng *et al.* from the Organic Materials Group of Prof. Shih-Ching Chuang, National Chiao Tung University, Faculty of Chemistry, Taiwan, Republic of China

Nucleophilic conjugate 1,3-addition of phosphines to oligoynoates

Herein we have elucidated unusual and unique nucleophilic conjugate 1,3-addition reactions of surveyed oligoynoates toward phosphines through spectroscopic and single crystal X-ray diffraction analyses of three-component reaction products of oligoynoates, phosphines and aldehydes.

As featured in:

See Shih-Ching Chuang *et al.*, *Chem. Commun.*, 2014, **50**, 10580.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Registered charity number: 207890

ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Nucleophilic conjugate 1,3-addition of phosphines to oligoynoates†

Cite this: *Chem. Commun.*, 2014, **50**, 10580

Received 18th April 2014,
Accepted 9th June 2014

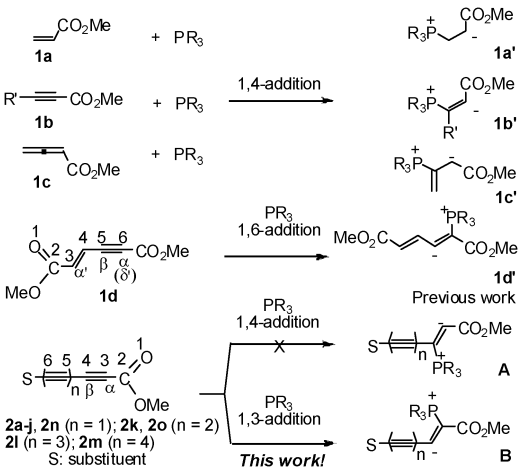
DOI: 10.1039/c4cc02870h

www.rsc.org/chemcomm

Jie-Cheng Deng,‡ Chih-Wei Kuo‡ and Shih-Ching Chuang*

Herein we have elucidated unusual and unique nucleophilic conjugate 1,3-addition reactions of surveyed oligoynoates toward phosphines through spectroscopic and single crystal X-ray diffraction analyses of three-component reaction products of oligoynoates, phosphines and aldehydes.

Nucleophilic conjugate addition, a unique class of nucleophilic reactions, is an important methodology in applied synthetic chemistry.[1] Numerous useful organic compounds can be prepared with conjugate addition reaction as a key step.[2] In this context, nucleophilic conjugate 1,*n*-addition (*n* = even number), for example, 1,2-, 1,4- or (β), 1,6- or (δ), and 1,8-addition patterns, has previously been observed due to resonance stabilization.[1] However, the 1,3-addition(α) pattern[3] is less common besides these even addition patterns.[4] The occurrence of an α-addition pattern could be attributed to either substitution of an electron-withdrawing moiety at β-carbon of alkenoates/alkynoates/nitro olefins[5] or through favoured 5-*exo-trig* cyclization taking place at α-carbon of a conjugated system.[6] Pioneering studies have focused on using β-trifluoromethyl substitution to alkenoates or alkynoates for increasing the electron positivity of α-carbon. Although Walborsky and Schwarz reported an unsuccessful attempt with a β-trifluoromethyl-substituted alkenoate,[7] Knunyants and Cheburkov later demonstrated a successful α-addition with a β-bis(trifluoromethyl)-substituted alkenoate substrate toward ammonia, amines and water nucleophiles.[5d] Rapoport and Klumpp also independently demonstrated other intramolecular and intermolecular 1,3-addition reactions with phenyl and trimethylsilyl-substituted ynamides, respectively.[5a,6a] Subsequently, a trifluoromethyl-substituted alkynone has also been demonstrated as another 1,3-addition acceptor by Bumgardner and Whangbo *et al.*[5b]



Scheme 1 Oligoynoates for testing nucleophilic conjugate 1,3-addition.

Chemists have been using the concept of 1,4-addition mode to account for the reaction mechanism of phosphines with electron-deficient alkenoates, allenoates and alkynoates (**1a–c**, Scheme 1),[8–14] evidenced by isolation of tetravalent phosphonium salt intermediates.[13a] A nucleophilic α-addition to alkynoates relevant to phosphine catalysis also used the classical 1,4-addition pathway to interpret the reaction mechanism.[15] Recently, we reported an unusual three-component reaction initiated by nucleophilic attack of phosphines at α(δ′)-carbon of an enyne **1d** to generate a 1,3-dipole **1d′**.[16] Based upon the IUPAC nomenclature, such nucleophilic attack is formally formulated as a 1,6-conjugate addition (δ-addition) since the alkenyl moiety is numbered with higher priority with respect to the alkynyl one. However, it has been evident that substitution at β-carbon of alkynoates with an alkenyl group alters the addition pattern. Other amine nucleophiles also reacted with **1d** to provide α(δ′)-addition products.[17] Further, we have noted that the addition pattern is substrate-dependent since displacement of the ester moiety on the alkynyl carbon of **1d** with an aryl group results in a normal 1,4-addition.[18] Our continuing interests in finding new π-electrophiles that could undergo conjugate addition at the

Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan, Republic of China. E-mail: jscchuang@faculty.nctu.edu.tw; Fax: +886-35723764; Tel: +886-35731858

† Electronic supplementary information (ESI) available. CCDC 901699, 901985, 902919 and 903961. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc02870h

‡ These authors contributed equally to this work.

formal α-position toward nucleophiles led us to evaluate regioreactivity of oligoynoates **2a–o**—the numbering of IUPAC or the Greek letter order by nomenclature of these investigated oligoynoates **2** will become parallel. Herein, we wish to report a new class of acceptors having oligoynyl units for nucleophilic conjugate 1,3-additions with phosphines to generate 1,3-dipole **B**, unequivocally evidenced by crystal structures of three-component reaction products with aldehydes.

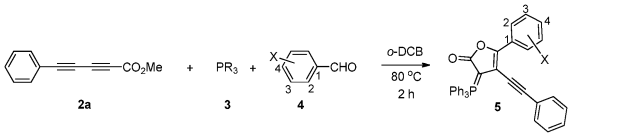
First, we prepared diynoates **2a–j** and **2n** (n = 1) through Hay coupling reactions and evaluated their reactivity toward phosphine nucleophiles. We selected diynoate **2a** as a model substrate for optimization of conditions (Table S1; see the ESI†). The investigated 1,3-addition three-component reaction gave optimized yields with a molar ratio of **2a** : **3a** : **4a** = 1.5 : 1.5 : 1.0 in *o*-dichlorobenzene (*o*-DCB) at 80 °C for 2 hours, giving lactone **5a** in 65% yield (entry 8). Other conditions with THF or dichloromethane as solvents (entries 1 and 2) and higher loading of **2a** and **3a** (entry 9) did not give much better yields.

The reaction scope study with variously substituted electron-donating and withdrawing phosphines (**3a–g**) and aromatic aldehydes (**4a–d**) also gave α-ylide lactone products **5a–u** through 1,3-addition reaction in 32–73% isolated yields (Table 1). The isolation of these α-phosphorus ylide lactones for characterization was highly dependent on the stability of **5**. We can only isolate **5** with triarylphosphine functionality for structural characterization because they were relatively more stable. Albeit trialkyl phosphines also promoted the reaction to occur, we were not able to isolate stable corresponding lactones for structural elucidation. It is noteworthy that reactive lactone **5g** with hexamethylphosphorus triamide (HMPT) can be isolated for characterization in a rush manner. These isolated lactones can be stored in their solid states at room temperature under anaerobic conditions for a few weeks.

To establish the scope of the 1,3-addition with variously substituted asymmetric diynoates, we further investigated the reaction of diynoates **2b–j** with selected phosphines (**3a–c** and **3f**) and aldehyde **4a**. The surveyed reactions proceeded through 1,3-addition to give lactone products **5** in decent to good isolated yields (32–73%, Table 2); lower reaction yields were observed in the cases of diynoates (**2b**, **2d** and **2f**) with the ethyl ester moiety (entries 1–3, 7–9 and 13–15; 33–49%) due to the poor leaving ability of ethoxide during lactonization. The reaction with terminally 4-*t*-butyl phenyl and methyl ester-capped diyne (**2c**) and P(*p*-tolyl)$_3$ (**3b**) gave the highest yield (entry 5, 73%) among all, and other halo or methoxy phenyl-substituted diynoates (**2e–j**) gave moderate yields (entries 10–19; 32–66%). These results further firmly supported the occurrence of 1,3-addition of phosphines in a range of aryl-substituted electron-donating and withdrawing diynoates.

We intended to alter the addition pattern through placement of additional alkynyl units and later noted that further extension of the acetylenic unit (C_2) on **2** (n = 2–4) resulted in the same 1,3-addition pattern with phosphines (Table 3). We used iterative Hay coupling for the syntheses of oligoynoates **2** (n = 2–4; see the ESI†). Initially, the testing of the reaction of oligoynoates **2k–l** with n = 2–4 was hampered by their infeasibleness for isolation. We observed that these oligoynoates became relatively unstable as the alkynyl units increased. For isolating these unstable oligoynoates, we avoided evaporation of the oligoynoates solution to dryness and determined their solution concentrations by ^{1}H NMR

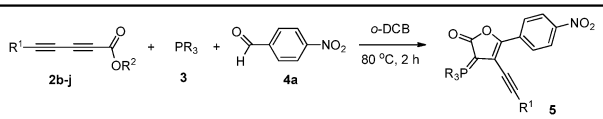
Table 1 Reaction scope of **2a** with phosphines and aldehydes[a]



Entry	PR_3 (**3**)	X (**4**)	Product **5**	Yield[b]
1	PPh_3 (**3a**)	4-NO_2 (**4a**)	**5a**	67
2	P(*p*-tolyl)$_3$ (**3b**)	4-NO_2 (**4a**)	**5b**	66
3	PPh_2(*p*-tolyl) (**3c**)	4-NO_2 (**4a**)	**5c**	73
4	P(4-OMe-Ph)$_3$ (**3d**)	4-NO_2 (**4a**)	**5d**	62
5	P(4-Cl-Ph)$_3$ (**3e**)	4-NO_2 (**4a**)	**5e**	58(60)
6	P(4-F-Ph)$_3$ (**3f**)	4-NO_2 (**4a**)	**5f**	47(52)
7[c]	HMPT (**3g**)	4-NO_2 (**4a**)	**5g**	41
8	PPh_3 (**3a**)	3-NO_2 (**4b**)	**5h**	58
9	P(*p*-tolyl)$_3$ (**3b**)	3-NO_2 (**4b**)	**5i**	64
10	P(4-OMe-Ph)$_3$ (**3d**)	3-NO_2 (**4b**)	**5j**	56
11	P(4-Cl-Ph)$_3$ (**3e**)	3-NO_2 (**4b**)	**5k**	49(52)
12	P(4-F-Ph)$_3$ (**3f**)	3-NO_2 (**4b**)	**5l**	51(55)
13	PPh_3 (**3a**)	4-Cl-3-NO_2 (**4c**)	**5m**	55
14	P(4-OMe-Ph)$_3$ (**3d**)	4-Cl-3-NO_2 (**4c**)	**5n**	52
15	P(4-F-Ph)$_3$ (**3f**)	4-Cl-3-NO_2 (**4c**)	**5o**	46(50)
16	PPh_3 (**3a**)	4-CN (**4d**)	**5p**	43
17	P(*p*-tolyl)$_3$ (**3b**)	4-CN (**4d**)	**5q**	58
18	PPh_2(*p*-tolyl) (**3c**)	4-CN (**4d**)	**5r**	61(85)
19	P(4-OMe-Ph)$_3$ (**3d**)	4-CN (**4d**)	**5s**	59
20	P(4-F-Ph)$_3$ (**3f**)	4-CN (**4d**)	**5t**	54(61)
21[c]	HMPT (**3g**)	4-CN (**4d**)	**5u**	32

[a] Reaction was carried out under anhydrous conditions unless otherwise noted; a molar ratio of **2a** : **3** : **4** = 1.5 : 1.5 : 1.0. [b] Isolated yields (%); yields in parentheses were determined based on converted aldehydes. [c] Reaction was carried out at room temperature.

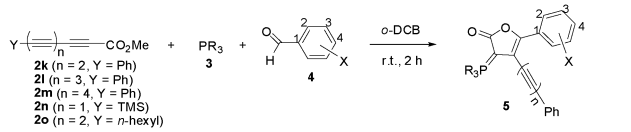
Table 2 Reaction scope with diynoates (**2b–j**)[a]



Entry	R^1	R^2	**2**	PR_3 (**3**)	**5**	Yield[b]
1	Ph	Et	**2b**	PPh_3 (**3a**)	**5a**	42
2	Ph	Et	**2b**	P(*p*-tolyl)$_3$ (**3b**)	**5b**	49
3	Ph	Et	**2b**	P(4-F-Ph)$_3$ (**3f**)	**5f**	48(54)
4	4-*t*-Bu-Ph	Me	**2c**	PPh_3 (**3a**)	**5v**	72
5	4-*t*-Bu-Ph	Me	**2c**	P(*p*-tolyl)$_3$ (**3b**)	**5w**	73
6	4-*t*-Bu-Ph	Me	**2c**	P(4-F-Ph)$_3$ (**3f**)	**5x**	63(70)
7	4-*t*-Bu-Ph	Et	**2d**	PPh_3 (**3a**)	**5v**	44
8	4-*t*-Bu-Ph	Et	**2d**	P(*p*-tolyl)$_3$ (**3b**)	**5w**	49
9	4-*t*-Bu-Ph	Et	**2d**	P(4-F-Ph)$_3$ (**3f**)	**5x**	39(44)
10	4-F-Ph	Me	**2e**	PPh_3 (**3a**)	**5y**	43(45)
11	4-F-Ph	Me	**2e**	P(*p*-tolyl)$_3$ (**3b**)	**5z**	48(50)
12	4-F-Ph	Me	**2e**	P(4-F-Ph)$_3$ (**3f**)	**5aa**	32(43)
13	4-F-Ph	Et	**2f**	PPh_3 (**3a**)	**5y**	39(41)
14	4-F-Ph	Et	**2f**	P(*p*-tolyl)$_3$ (**3b**)	**5z**	42
15	4-F-Ph	Et	**2f**	P(4-F-Ph)$_3$ (**3f**)	**5aa**	33
16	2-Cl-Ph	Me	**2g**	PPh_2(*p*-tolyl) (**3c**)	**5ab**	60(70)
17	3-Cl-Ph	Me	**2h**	PPh_2(*p*-tolyl) (**3c**)	**5ac**	66(72)
18	4-Cl-Ph	Me	**2i**	PPh_2(*p*-tolyl) (**3c**)	**5ad**	47(52)
19	4-OMe-Ph	Me	**2j**	PPh_2(*p*-tolyl) (**3c**)	**5ae**	33(49)

[a] Reaction was carried out under anhydrous conditions unless otherwise noted; a molar ratio of **2** : **3** : **4a** = 1.5 : 1.5 : 1.0. [b] Isolated yields (%); yields in parentheses were determined based on converted aldehydes.

Table 3 Reaction scope of oligoynoates (**2a**, **2k–o**) with phosphines and aldehydes[a]



entry	2	PR_3 (3)	X (4)	5	Yield[b]
1	**2k**	PPh_3 (**3a**)	4-NO_2 (**4a**)	**5af**	68
2	**2k**	$P(p\text{-tolyl})_3$ (**3b**)	4-NO_2 (**4a**)	**5ag**	67
3	**2k**	$PPh_2(p\text{-tolyl})$ (**3c**)	4-NO_2 (**4a**)	**5ah**	69
4	**2k**	$P(4\text{-OMe-Ph})_3$ (**3d**)	4-NO_2 (**4a**)	**5ai**	41
5	**2k**	$P(4\text{-Cl-Ph})_3$ (**3e**)	4-NO_2 (**4a**)	**5aj**	62(73)
6	**2k**	$P(4\text{-F-Ph})_3$ (**3f**)	4-NO_2 (**4a**)	**5ak**	73
7	**2k**	PPh_3 (**3a**)	3-NO_2 (**4b**)	**5al**	60
8	**2k**	$P(p\text{-tolyl})_3$ (**3b**)	3-NO_2 (**4b**)	**5am**	55
9	**2k**	$PPh_2(p\text{-tolyl})$ (**3c**)	3-NO_2 (**4b**)	**5an**	60(64)
10	**2k**	$P(4\text{-OMe-Ph})_3$ (**3d**)	3-NO_2 (**4b**)	**5ao**	54
11	**2k**	$P(4\text{-Cl-Ph})_3$ (**3e**)	3-NO_2 (**4b**)	**5ap**	46(64)
12	**2k**	$P(4\text{-F-Ph})_3$ (**3f**)	3-NO_2 (**4b**)	**5aq**	62(65)
13	**2l**	PPh_3 (**3a**)	4-NO_2 (**4a**)	**5ar**	36
14	**2l**	$P(p\text{-tolyl})_3$ (**3b**)	4-NO_2 (**4a**)	**5as**	35
15	**2l**	$PPh_2(p\text{-tolyl})$ (**3c**)	4-NO_2 (**4a**)	**5at**	38(50)
16	**2l**	$P(4\text{-OMe-Ph})_3$ (**3d**)	4-NO_2 (**4a**)	**5au**	43
17	**2l**	$P(4\text{-Cl-Ph})_3$ (**3e**)	4-NO_2 (**4a**)	**5av**	28(47)
18	**2l**	$P(4\text{-F-Ph})_3$ (**3f**)	4-NO_2 (**4a**)	**5aw**	39(62)
19[c]	**2m**	PPh_3 (**3a**)	4-NO_2 (**4a**)	**5ax**	32
20[d]	**2n**	$PPh_2(p\text{-tolyl})$ (**3c**)	4-CN (**4d**)	**5ay**	48
21	**2o**	$P(p\text{-tolyl})_3$ (**3b**)	4-NO_2 (**4a**)	**5az**	66
22	**2o**	$PPh_2(p\text{-tolyl})$ (**3c**)	3-NO_2 (**4b**)	**5aaa**	72
23	**2a**	PPh_3 (**3a**)	H (**4e**)	**5aab**	10(18)

[a] Reaction was carried out under anhydrous conditions unless otherwise noted; a molar ratio of **2** : **3** : **4** = 1.5 : 1.5 : 1.0. [b] Isolated yields (%); yields in parentheses were determined based on converted aldehydes. [c] Reaction was carried out *via* slow addition of **2m** in 8 h with **2m** : **3a** : **4a** = 1.0 : 1.1 : 4.1. [d] 10% of TMS deprotected lactone **5ay′** was isolated after chromatography (see data in ESI).

spectroscopy instantly after silica gel chromatography. Despite that oligoynoates (**2k–m**) can be stored in *o*-DCB solution at 0 °C for a few days, their solutions turned brown in colour soon at room temperature likely due to intermolecular stacking aggregation. For their higher reactivity, we immediately carried out the reactions with triynoate (**2k**) and tetraynoate (**2l**) at room temperature (25 °C) and that with pentaynoate (**2m**) at 0 °C right after they were purified (Table 3). According to these data, we observed formation of lactones **5** through 1,3-addition up to 73 and 62% isolated yields (entries 6 and 12) with reactant combinations of triynoate (**2k**)/phosphine (**3f**)/aldehyde (**4a**) and triynoate (**2k**)/phosphine (**3f**)/aldehyde (**4b**), respectively. The isolated yields decreased as the alkynyl units of **2** increased—we observed optimal 43 and 39% yields with tetraynoate **2l** (entries 16 and 18; **2l**/**3d**/**4a** and **2l**/**3f**/**4a**), and 32% with pentaynoate **2m** (entry 19, **2m**/**3a**/**4a**), respectively. It is worth noting that reactions with these oligoynoates at higher temperature led to poor yields due to decomposition of either oligoynoates or products. The scope of this reaction can be further extended to TMS-capped diynoate (**2n**) and *n*-hexyl-capped triynoate (**2o**), yielding corresponding lactones **5ay**, **5az** and **5aaa** respectively (entries 20–22). We further observed decreasing reactivity toward aldehydes with an electron-donating moiety and aliphatic aldehyde—reactions with benzaldehyde provided only 10% **5aab** and those with *p*-tolualdehyde and decanal resulted in the recovery of aldehydes in 97 and 85% respectively. In these two cases, the generated reactive intermediates may react with oligoynoates to form polymeric materials, as highly polar black-brown coloured materials were observed by column chromatography.

The isolated α-phosphorus ylide lactones **5** were characterized by spectroscopic methods (IR; ^{1}H, ^{13}C and ^{31}P NMR) and can be recrystallized for X-ray crystallographic analyses. The selected solid state structures of **5b**, **5ak**, **5ar**, and **5ax** (Fig. 1) unambiguously demonstrated the covalent bonding of the phosphorus atom to the α-carbon adjacent to the carbonyl moiety, confirming the existence of the 1,3-addition pattern of these oligoynoates **2** with phosphines.[19] We accounted for the formation of ylide **5** by the initial nucleophilic attack of phosphine PR_3 at α-carbon of oligoynoates **2a–o** (Scheme 2) to generate reactive zwitterionic species **Ia** having a carbanion at β-carbon. Direct addition of **Ia** to carbonyl carbon of aldehydes followed by intramolecular cyclization provided **Ic** (*via* intermediate **Ib**). Then, product **5** was formed through deprotonation of **Id** by a released alkoxide. In this proposed pathway, the generated reactive intermediate **Ia** may choose to undergo nucleophilic addition to oligoynoates **2a–o** and form polymeric materials. In the absence of aldehydes, a similar notion was observed after mixing oligoynoates and phosphines in solution.

In light of the current results, formation of lactone products through initial 1,3-addition of phosphines to these investigated

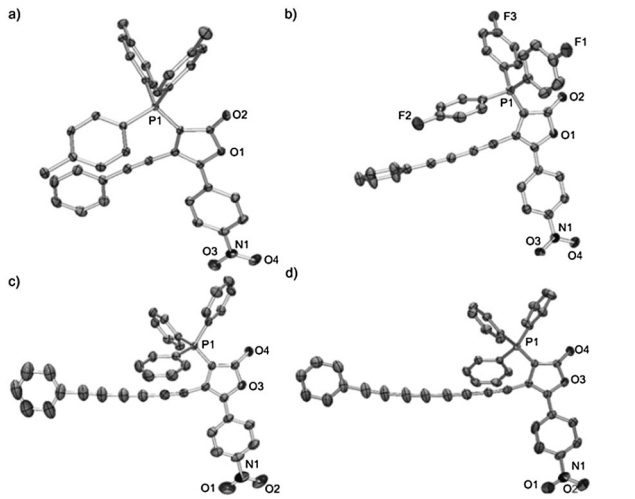
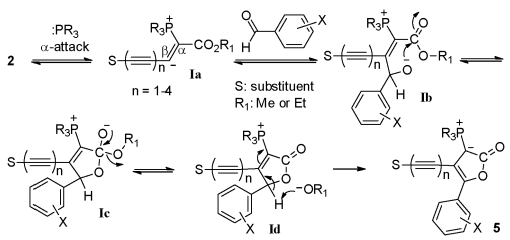


Fig. 1 Thermal ellipsoids of crystallized compounds (a) **5b**, (b) **5ak**, (c) **5ar** and (d) **5ax** with solvents omitted for clarity.



Scheme 2 Proposed mechanism for formation of **5**.

oligoynoates is inferred. We could not exclude the likelihood of the occurrence of 1,4-addition although we did not isolate the corresponding products. The putative 1,4-addition pathway may result in the formation of unstable intermediates which proceed to regenerate reactants followed by 1,3-addition or undergo polymerization with oligoynoates. The preliminary computational studies of these oligoynoates exhibited larger orbital coefficients along P_z at the α-carbon of **2**,[20] corroborating the currently observed 1,3-addition with phosphine nucleophiles. Other mechanistic consideration leading to 1,3-addition such as the oxophilicity of phosphines and resonance stabilization through an alkynyl π-moiety also cannot be excluded.

In summary, we have demonstrated a unique nucleophilic conjugate 1,3-addition reaction of oligoynoates with phosphines through analyses of their assembled products with aldehydes. Extension of the acetylenic unit does not alter the addition pattern. The novel addition mode represents the first formal α-selective nucleophilic conjugate reaction of phosphines to oligoynoates. This new class of acceptors may be applicable as reaction partners for other Morita–Baylis–Hillman type reactions. Our ongoing endeavors are directed to explore the regioreactivity of these oligoynoates toward other organometallic and organic nucleophiles such as N-heterocyclic carbenes (NHC). Application of this phosphine 1,3-addition reaction toward syntheses of useful products and toward phosphine catalysis is also underway.[21]

We thank the Ministry of Science and Technology of Taiwan for supporting this research financially (MOST101-2113-M-009-008).

Notes and references

1 J. March, *Advanced Organic Chemistry*, Wiley, New York, 4th edn, 1992.
2 M. B. Smith, *Organic Synthesis*, McGRAW-HILL, INC, New York, 1994.
3 For a review, see: E. Lewandowska, *Tetrahedron*, 2007, **63**, 2107 and relevant references therein.
4 M. E. Jung, in *Organic Synthesis*, ed. M. Trost, I. Fleming and M. F. Semmelhack, Pergamon, Oxford, 1991, vol. 4, pp. 1–67.
5 (*a*) G. W. Klumpp, A. J. C. Mierop, J. J. Vrielink, A. Brugman and M. Schakel, *J. Am. Chem. Soc.*, 1985, **107**, 6740; (*b*) C. L. Bumgardner, J. E. Bunch and M.-H. Whangbo, *J. Org. Chem.*, 1986, **51**, 4082; (*c*) A. Kamimura, H. Sasatani, T. Hashimoto, T. Kawai, K. Hori and N. Ono, *J. Org. Chem.*, 1990, **55**, 2437; (*d*) I. L. Knunyants and Yu. A. Cheburkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1960, 2162; (*e*) J. Alemán, E. Reyes, B. Richter, J. Overgaard and K. A. Jørgensen, *Chem. Commun.*, 2007, 3921; (*f*) X. Bi, J. Zhang, Q. Liu, J. Tan and B. Li, *Adv. Synth. Catal.*, 2007, **349**, 2301; (*g*) R. Ballini, N. A. Bazan, G. Bosica and A. Palmieri, *Tetrahedron Lett.*, 2008, **49**, 3865.
6 (*a*) S. H. Rosenberg and H. Rapoport, *J. Org. Chem.*, 1985, **50**, 3979; (*b*) Y. Li, F. Liang, X. Bi and Q. Liu, *J. Org. Chem.*, 2006, **71**, 8006; (*c*) Y. Li, X. Xu, J. Tan, P. Liao, J. Zhang and Q. Liu, *Org. Lett.*, 2010, **12**, 244; (*d*) Y. F. Suen, H. Hope, M. H. Nantz, M. J. Haddadin and M. J. Kurth, *Tetrahedron Lett.*, 2006, **47**, 7893; (*e*) W.-D. Rudorf and R. Schwarz, *Synlett*, 1993, 369.
7 H. M. Walborsky and M. Schwarz, *J. Am. Chem. Soc.*, 1953, **75**, 3241.
8 (*a*) L.-W. Ye, J. Zhou and Y. Tang, *Chem. Soc. Rev.*, 2008, **37**, 1140; (*b*) J. L. Methot and W. R. Roush, *Adv. Synth. Catal.*, 2004, **346**, 1035; (*c*) X. Lu, Y. Du and C. Lu, *Pure Appl. Chem.*, 2005, **77**, 1985; (*d*) Y. C. Fan and O. Kwon, *Chem. Commun.*, 2013, **49**, 11588.
9 (*a*) X. Lu, C. Zhang and Z. Xu, *Acc. Chem. Res.*, 2001, **34**, 535; (*b*) C. Zhang and X. Lu, *J. Org. Chem.*, 1995, **60**, 2906.
10 Selected examples see: (*a*) S. W. Smith and G. C. Fu, *J. Am. Chem. Soc.*, 2009, **131**, 14231; (*b*) Y.-Q. Fang and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2008, **130**, 5660; (*c*) A. Voituriez, A. Panossian, N. Fleury-Bregeot, P. Retailleau and A. Marinetti, *J. Am. Chem. Soc.*, 2008, **130**, 14030; (*d*) B. J. Cowen and S. J. Miller, *J. Am. Chem. Soc.*, 2007, **129**, 10988; (*e*) R. P. Wurz and G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 12234.
11 J.-C. Wang and M. J. Krische, *Angew. Chem., Int. Ed.*, 2003, **42**, 5855.
12 S. A. Frank, D. J. Mergott and W. R. Roush, *J. Am. Chem. Soc.*, 2002, **124**, 2404.
13 (*a*) H. Guo, Q. Xu and O. Kwon, *J. Am. Chem. Soc.*, 2007, **129**, 6722; (*b*) G. S. Creech and O. Kwon, *Org. Lett.*, 2008, **10**, 429.
14 (*a*) Y. Xia, Y. Liang, Y. Chen, M. Wang, L. Jiao, F. Huang, S. Liu, Y. Li and Z.-X. Yu, *J. Am. Chem. Soc.*, 2007, **129**, 3470; (*b*) L.-C. Wang, A. L. Luis, K. Agapiou, H.-Y. Jang and M. J. Krische, *J. Am. Chem. Soc.*, 2002, **124**, 2402; (*c*) J. Ma, P. Xie, C. Hu, Y. Huang and R. Chen, *Chem. – Eur. J.*, 2011, **17**, 7418.
15 B. M. Trost and G. R. Dake, *J. Am. Chem. Soc.*, 1997, **119**, 7595.
16 (*a*) J.-C. Deng and S.-C. Chuang, *Org. Lett.*, 2011, **13**, 2248; (*b*) S.-C. Chuang, J.-C. Deng, F.-W. Chan, S.-Y. Chen, W.-J. Huang, L.-H. Lai and V. Rajeshkumar, *Eur. J. Org. Chem.*, 2012, 2606; (*c*) Y.-W. Lin, J.-C. Deng, Y.-Z. Hsieh and S.-C. Chuang, *Org. Biomol. Chem.*, 2014, **12**, 162.
17 A. S. Chavan, J.-C. Deng and S.-C. Chuang, *Molecules*, 2013, **18**, 2611.
18 P.-Y. Tseng and S.-C. Chuang, *Adv. Synth. Catal.*, 2013, **355**, 2165.
19 CCDC 901699, 901985, 902919 and 903961 contain the ESI† for **5b**, **5ak**, **5ar** and **5ax**.
20 Complete computational aspects of these oligoynoates will be reported elsewhere.
21 Some of the products are highly fluorescent; for example, lactone **5s** exhibits yellow-green fluorescence with a quantum yield of 0.91. Upon being equipped with appropriate chelating functionality, these lactones are effective metal ion chemosensors.