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A facile route to *cis*-olefin-linked phosphino-phosphonium salts of the form: $[Ph_2PC(R)C(H)P(R')_2H][AlCl_4]$

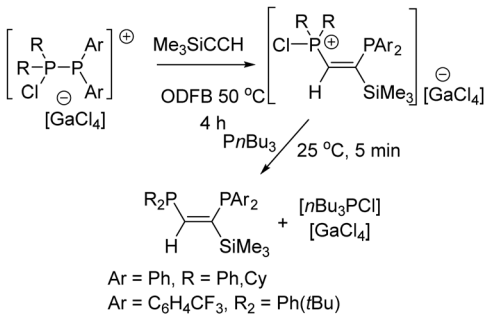
Nahil Al-Zuhaika,[a] Simon Severin,[ab] Madeleine D. Schmuckler,[a] Alan J. Lough[a] and Douglas W. Stephan *[a]

The diphenylphosphirenium salts of the form $[Ph_2PC(R)C(H)][AlCl_4]$ are readily generated and select examples react with secondary phosphines, R_2PH, to give dissymmetric bidentate phosphonium salts, $[Ph_2PC(R)C(H)P(R')_2H][AlCl_4]$. While these reactions work well for sterically encumbered combinations of the phosphirenium cations and secondary phosphines (R = *t*Bu, Cy, Mes), less encumbered combinations provide a mixture of products arising from alkyne displacement. As expected the protonated bis-phosphine salts are easily deprotonated, demonstrating easy access to a rare class of dissymmetric bidentate phosphine ligands.

From the advent of organometallic chemistry and the development of homogeneous catalysts in 1960s, phosphines have been a dominant class of ligands that have been widely employed. While simple monodentate phosphines were used initially, chelating bidentate phosphines emerged to provide additional complex stability by the chelate effect.[1] Subsequent modifications to introduce optically pure chiral centers were essential to the successful implementation of catalytic asymmetric reductions.[2–6] While modifications of the substituents on monodentate phosphines are achieved by treatment of phosphorus halides with selected organic nucleophiles, similar control of the substituents on bidentate ligands is more challenging. Thus, the vast majority of commercially available bidentate ligands incorporate two PPh_2 groups, while a few bidentate phosphines include two P-centers with substituents other than Ph groups.[1] Rarer still, are bidentate phosphines that incorporate differing phosphine fragments. Such ligands are very challenging to prepare by known methods as such dissymmetric bidentate phosphines typically require consecutive additions of differing phosphide nucleophiles,[7–10] or require metal catalyzed, photochemical or radical based reaction methods.[11–20]

In a recent effort targeting new routes to dissymmetric bidentate phosphines, we[21,22] recognized that the phosphino-phosphenium cation (PPC) originally described by Burford and coworkers[23–27] and others[28,29] can act as frustrated Lewis pairs (FLPs) and provide access to both phosphorus Lewis acidic and basic sites. As such, they undergo addition to alkynes to afford *cis*-substituted olefins to give cations of the form $[cis\text{-}R_3PCHC(R'')PR'_2]^+$.[21] Suitable modification of the precursors afforded $[cis\text{-}R_2ClPCHC(R'')PR'_2]^+$ which were readily reduced by nBu_3P to give the dissymmetric bidentate phosphine in good yields (Scheme 1).[21]

While this new protocol provides access to a rare set of bidentate phosphines, we sought to further improve the generality and facility of the synthetic protocol. We recognized that one of the limitations of the above method is the need for reduction of the intermediate phosphorus(v) halide salt (Scheme 1). We envisioned deprotonation as a simpler, cheaper process. Moreover, this avenue offers increased variability as a broad selection of secondary phosphines are commercially available. However, we also recognized that the reactivity of PPCs prepared using a secondary phosphine as the donor are readily deprotonated affording the neutral diphosphine $R_2PPR'_2$. Our previous mechanistic study revealed that phosphino-phosphination was initiated by alkyne displacement of the phosphine



Scheme 1 Previously reported FLP synthesis of dissymmetric bidentate phosphines. ODFB = $o\text{-}F_2C_6H_4$.

[a] *Department of Chemistry, University of Toronto, 80 St. George St, Toronto, ON, M5S3H6, Canada. E-mail: dstephan@chem.utoronto.ca*

[b] *Institute of Inorganic and Analytical Chemistry, University of Münster, Muenster, Germany*

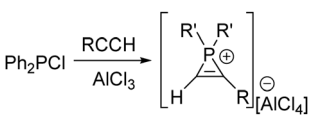
donor in the PPC generating a three membered phosphirenium cationic ring,[21] which undergoes subsequent ring opening by the chlorophosphines. Herein, we explore the reactivity of phosphirenium cations targeting ring-opening by secondary phosphines as a route to protonated dissymmetric bidentate phosphine cations, species which are readily deprotonated to give olefin-linked dissymmetric bidentate phosphines.

To initiate this study, the phosphirenium salt of the form $[R_2P(R'CCH)][AlCl_4]$ were prepared according to literature procedures[30–34] *via* a 1 : 1 : 1 reaction of the chlorodiphenylphosphine, terminal alkyne and $AlCl_3$ (Table 1). Initially using *t*BuCCH, the species $[Ph_2PC(tBu)C(H)][AlCl_4]$ **1** was generated as evidenced by the ^{31}P NMR signal at 104.6 ppm, characteristic of the phosphirenium cation.

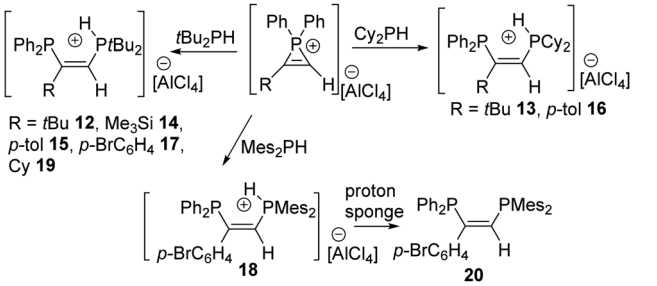
In a similar fashion, this protocol was used to generate a series of related phosphirenium cations $[Ph_2PC(R)C(H)][AlCl_4]$ (R = $SiMe_3$ **2**, Ph **3**, *p*-tol **4**, *p*-(HCC)C_6H_4 **5**, *p*-IC_6H_4 **6**, *p*-BrC_6H_4 **7**, C_4H_9 **8**, C_3H_5 **9**, C_5H_9 **10**, C_6H_{11} **11**). While these species were not isolated all reactions showed a clean singlet in the ^{31}P NMR spectrum in the range of 104–122 ppm, typical of phosphirenium cations.

As these phosphirenium cations proved to be readily generated, we next assessed the ability of a secondary phosphine to effect ring opening of these phosphacyclic cations. To this end, we first generated a CH_2Cl_2 solution of **1** and added an equivalent of tBu_2PH. Stirring the mixture 20 minutes followed by subsequent workup afforded a reddish-brown sticky solid **12** in 85% yield. This species shows a $^{31}P\{^1H\}$ NMR spectrum consisting of two doublets at 28.6 and −1.1 ppm with a coupling constant of 86 Hz. The corresponding ^{31}P NMR spectrum revealed that the downfield signal also showed P–H coupling of 474 Hz consistent with a one-bond P–H coupling constant. Thus, the upfield resonance was attributed to a PPh_2-fragment, while the downfield signal was assigned to the protonated tBu_2PH-fragment. These data together with ^1H NMR and MS data supported the formulation of **12** as $[Ph_2PC(tBu)C(H)(HPtBu_2)][AlCl_4]$ (Scheme 2). On standing slow vaporization of CH_2Cl_2 from the reaction mixture provided crystals of **12** suitable for an XRD study. The structural data

Table 1 Generation of phosphirenium cation salts



Cmpd	R	*T* (h)	Solvent	^{31}P shift
1	*t*Bu	0.3	CH_2Cl_2	−104.6
2	Me_3Si	1	CH_2Cl_2	−122.0
3	Ph	94	*o*-DFB	−105.5
4	*p*-tol	0.3	CH_2Cl_2	−107.3
5	*p*-(HCC)C_6H_4	24	*o*-DFB	−105.9
6	*p*-IC_6H_4	48	CH_2Cl_2	−106.2
7	*p*-BrC_6H_4	0.3	CH_2Cl_2	−105.8
8	C_4H_9	95	*o*-DFB	−106.9
9	*c*-C_3H_5	0.5	CH_2Cl_2	−105.8
10	*c*-C_5H_9	2	C_6H_5Me	−107.2
11	Cy	1	CH_2Cl_2	−107.2



Scheme 2 Synthesis of **12–20**.

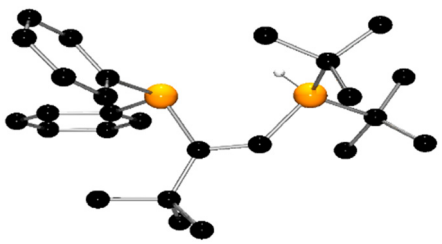


Fig. 1 POV-ray depiction of the crystallographic structure of the cation of **12**. Hydrogen atoms except for the PH unit are omitted for clarity. C: black, P: orange, H: white.

confirmed the formulation of the salt **12** (Fig. 1) in which cation and anion are well separated. In the cation, the phosphorus centers adopt a *cis*-disposition with P–C bond distances to the linking olefinic fragment found to be 1.847(6) Å and 1.793(6) Å. The shorter of the two is associated with the cationic tBu_2PH fragment. Despite the phosphonium center, the tBu_2PH fragment affords the shorter P–C bond, consistent with the presence of the electron donating alkyl substituents and the less hindered carbon center. The olefin linker showed the typical C–C distance of 1.336(9) Å.

In a similar fashion following this protocol, reaction of **1** with Cy_2PH, afforded a sticky solid in 73% yield. This product **13** showed $^{31}P\{^1H\}$ NMR resonances at 9.5 and −2.8 ppm with a P–P coupling constant of 57 Hz. The corresponding ^1H coupled ^{31}P NMR data revealed the downfield signal was also coupled to proton with a coupling constant of 479 Hz. These data as well as mass spectral data affirmed the formulation of **13** as $[Ph_2PC(tBu)C(H)(HPCy_2)][AlCl_4]$ (Scheme 2).

In the case of the analog using the phosphirenium salt **2**, reaction with tBu_2PH was performed on a 2 g scale following a similar procedure. The ultimate yield of the $[Ph_2PC(Me_3Si)C(H)(HPtBu_2)][AlCl_4]$ **14** was 91% yield (Scheme 2). This species showed the two expected resonances in the $^{31}P\{^1H\}$ NMR spectrum at 20.9 and −3.39 ppm with a $^3J_{PP}$ of 81 Hz, while the ^{31}P NMR spectrum revealed a $^1J_{PH}$ of 466 Hz for the upfield resonance, again consistent with the formation of **14**.

We next examined the reactions of related aryl-substituted phosphirenium cations. Thus, **4** was independently reacted with tBu_2PH or Cy_2PH. These reactions proceeded similar to those above affording reddish-brown and yellowish-orange products **15** and **16**. These products were further purified by

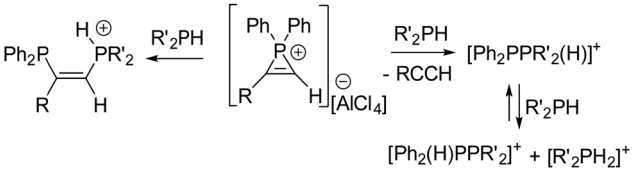
reprecipitation from C_6H_5Cl and isolated in 89% and 62% yields respectively. Compound **15** exhibited ^{31}P resonances at 26.6 and −4.5 ppm with $^3J_{PP}$ of 74 Hz and the downfield signal exhibiting a $^1J_{PH}$ of 461 Hz. The corresponding data for **16** showed ^{31}P signals at 9.6 and −2.6 ppm with $^3J_{PP}$ of 70 Hz with the downfield signals also exhibiting 475 Hz, respectively. These data again affirmed the formulation of these products as $[Ph_2PC(p\text{-tol})C(H)(HPR_2)][AlCl_4]$ (R = *t*Bu **15**, Cy **16**) (Scheme 2).

Switching the phosphirenium cation to **7**, the corresponding derivative $[Ph_2PC(p\text{-}BrC_6H_4)C(H)(HPtBu_2)][AlCl_4]$ **17** was formed in 76% yield (Scheme 2) as evidenced by the ^{31}P resonances at 27.0 and −4.0 ppm with $^3J_{PP}$ and $^1J_{PH}$ of 77 and 450 Hz, respectively. While this formulation was also supported by ^1H and MS data (see SI) it was also supported by a crystallographic study. This unambiguously confirmed the formation of **17** where two phosphorus atoms on an olefinic linker are *cis*-disposed (Fig. 2). Further the PPh_2 fragment resides on the substituted carbon of the olefinic link, and the $PtBu_2$ fragment is protonated. The resulting P–C bond distances to the linking olefin were found to be 1.862(2) Å and 1.780(2) Å, with the shorter P–C bond arising from tBu_2P-fragment. The remainder of the metric parameters are unexceptional.

In a similar fashion reaction of **7** with Mes_2PH gave an orange-yellow solid in 91% yield. Two ^{31}P resonances at −2.3 and −31.6 ppm showed a $^3J_{PP}$ of 100 Hz and the upfield signals showed a $^1J_{PH}$ of 497 Hz, consistent with the formulation of **18** as $[Ph_2PC(p\text{-}BrC_6H_4)C(H)(HPMes_2)][AlCl_4]$ (Scheme 2) which was also supported by ^1H and MS data (see SI).

Probing the generality of this reactivity further, the corresponding reaction of **7** with Ph(*t*Bu)PH was found to give a complex mixture of products including unreacted phosphirenium cation, the expected product $[Ph_2PC(p\text{-}BrC_6H_4)C(H)(HP(tBu)(Ph)][AlCl_4]$, $[Ph_2P(PHPh(tBu))]^+$, $[Ph(tBu)P(PHPh_2)]^+$ and $[H_2P(tBu)(Ph)]^+$ (Scheme 3) as evidenced by the ^{31}P NMR signals. The complexity of this mixture precluded the isolation of individual products, but did provide some mechanistic insights.

The product mixture is consistent with two reaction pathways. Reaction of the phosphirenium cation with Ph(*t*Bu)PH can proceed *via* ring-opening to protonated bisphosphine salt,



Scheme 3 Divergent reaction pathways for less hindered combinations of phosphirenium cations and secondary phosphines.

alternatively alkyne displacement affords phosphino-phosphenium cations which in the presence of secondary phosphine also generates $[H_2P(tBu)(Ph)]^+$. We note that no evidence of this latter pathway was seen in the previous examples where either bulky substituents were incorporated into the secondary phosphine or the alkyne. These observations can be rationalized on the basis of steric demands associated with the nucleophilic attack of the phosphirenium cation as well as the basicity of the alkyne used to generate the phosphirenium cation. While sterically demanding secondary phosphines lead to attack at the unsubstituted carbon of the phosphirenium cation, sterically less encumbered phosphines can access the σ*-orbital on phosphorus, prompting alkyne displacement and the formation of phosphino-phosphenium cations.

To further probe this notion, the phosphirenium salt **11** was reacted with tBu_2PH affording the dissymmetrically substituted $[Ph_2PC(Cy)C(H)(HPtBu_2)][AlCl_4]$ **19** (Scheme 2) as evidenced by the ^{31}P NMR signals at 28.5 and −6.5 ppm with a P–P coupling constant of 93 Hz and the P–H coupling of the downfield signal of 474 Hz. In contrast, reaction of **11** with the less sterically encumbered Cy_2PH generated a mixture of products including $[Ph_2PPCy_2H]^+$, $[Ph_2PHPCy_2]^+$ and $[Cy_2PH_2]^+$ (see SI) as evidenced by ^{31}P NMR spectroscopy (Scheme 3).

Collectively, these data affirm that less hindered combinations of phosphirenium cations and secondary phosphines react *via* divergent pathways to afford a mixture of products. On the other hand, more sterically demanding systems are shown to readily afford protonated, dissymmetrically substituted, olefin-linked phosphino-phosphonium cations **12–19**. To confirm that such cations can be deprotonated in a trivial fashion, compound **18** was treated with an equivalent of 1,8-bis(dimethylamino)-naphthalene (proton sponge) for 30 minutes.

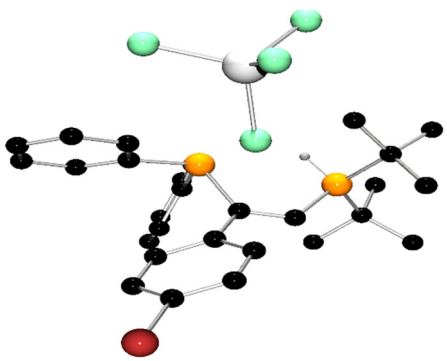


Fig. 2 POV-ray depiction of the crystallographic structure of **17**. Hydrogen atoms except for the PH unit are omitted for clarity. C: black, P: orange, Cl: green, Al: white, Br: red.

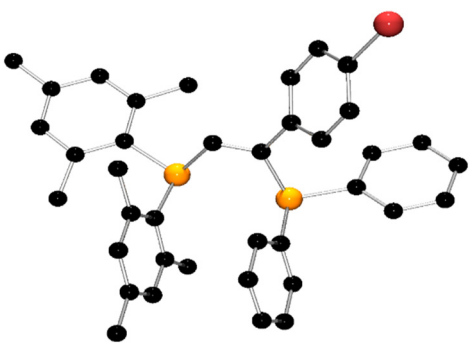


Fig. 3 POV-ray depiction of the crystallographic structure of **20**. Hydrogen atoms are omitted for clarity. C: black, P: orange, Br: red.

Following solvent removal under vacuum, the product **20** (Scheme 2) was obtained in a 90% yield. The ^{31}P NMR spectrum of **20** shows resonances at −7.6 and −35.5 ppm with a coupling constant of 148 Hz consistent with the formulation of **20** as the bidentate phosphine, $Ph_2PC(p\text{-}BrC_6H_4)C(H)(PMes_2)$. This formulation was also confirmed *via* a crystallographic study (Fig. 3). The *cis*-bisphosphine and dissymmetric nature of **20** revealed P–C distances to the linking olefinic fragment of 1.841(4) Å and 1.824(4) Å for the $PMes_2$ and PPh_2 fragments respectively, with a C=C bond length of 1.349(6) Å.

Herein, we demonstrated that the salts $[Ph_2PC(R)CH][AlCl_4]$ are readily generated using a variety of terminal alkynes. The reactions of such species with secondary phosphines showed that less encumbered combinations give rise to mixtures of ring-opened and alkyne displacement products, while bulkier combinations afford exclusively the ring-opening products, $[Ph_2PC(R)C(H)PR'_2H][AlCl_4]$. Facile deprotonation affording a dissymmetric bidentate phosphine ligand was demonstrated confirming that this new synthesis route provides ready access to a class of compounds that are generally rare and otherwise challenging to prepare. We are continuing to examine the reactions of phosphirenium cations as well as new strategies to desirable phosphorus-based compounds.

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NA, SS and MDS performed the experimental work, AL performed one of the X-ray structural studies while DWS wrote the manuscript. All authors edited the draft.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included in the SI. Supplementary information: Synthetic details and spectral data. See DOI: **https://doi.org/10.1039/d5cc03456f**.

CCDC 2444558 (**17**), 2444559 (**12**) and 2444560 (**20**) contain the supplementary crystallographic data for this paper.[35–37]

Notes and references

1 A. L. Clevenger, R. M. Stolley, J. Aderibigbe and J. Louie, *Chem. Rev.*, 2020, **120**, 6124–6196.
2 T. Colacot, *Chem. Eng.*, 2001, **108**, 73–74.
3 A. Marinetti and D. Brissy, *Catal. Met. Complexes*, 2011, **37**, 305–341.
4 S. Chakrabortty, A. A. Almasalma and J. G. de Vries, *Catal. Sci. Technol.*, 2021, **11**, 5388–5411.
5 A. Sen and S. H. Chikkali, *Org. Biomol. Chem.*, 2021, **19**, 9095–9137.
6 J. Vondran, M. R. L. Furst, G. R. Eastham, T. Seidensticker and D. J. Cole-Hamilton, *Chem. Rev.*, 2021, **121**, 6610–6653.
7 H. Brunner, M. Muschiol and M. Zabel, *Synthesis*, 2008, 405–408.
8 D. J. Gulliver and W. Levason, *Inorg. Chim. Acta*, 1981, **54**, L15–L16.
9 M. O. Shulyupin, E. A. Chirkov, M. A. Kazankova and I. P. Beletskaya, *Synlett*, 2005, 658–660.
10 J. Ye, J.-Q. Zhang, Y. Saga, S.-Y. Onozawa, S. Kobayashi, K. Sato, N. Fukaya and L.-B. Han, *Organometallics*, 2020, **39**, 2682–2694.
11 J. L. Bookham and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1990, 489, DOI: **10.1039/dt9900000489**.
12 A. Kondoh, H. Yorimitsu and K. Oshima, *J. Am. Chem. Soc.*, 2007, **129**, 4099–4104.
13 H. X. Li, L. L. Zhao, G. Lu, Y. R. Mo and Z. X. Wang, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5268–5275.
14 K. A. Lotsman, K. S. Rodygin, I. Skvortsova, A. M. Kutskaya, M. E. Minyaev and V. P. Ananikov, *Org. Chem. Front.*, 2023, **10**, 1022–1033.
15 J. Ma, H. Fan, B. Hao, Y. Jiang, L. Wang, X. Wang, J. Zhang and T. Jiang, *J. Catal.*, 2022, **413**, 1–7.
16 X. Ma, H. Wang, Y. Liu, X. Zhao and J. Zhang, *ChemCatChem*, 2021, **13**, 5134–5140.
17 B. Demerserman, P. L. Coupanec and P. H. Dixneuf, *J. Organomet. Chem.*, 1985, **287**, C35–C38.
18 S. Kawaguchi, S. Nagata, T. Shirai, K. Tsuchii, A. Nomoto and A. Ogawa, *Tetrahedron Lett.*, 2006, **47**, 3919–3922.
19 Y. Sato, M. Nishimura, S. I. Kawaguchi, A. Nomoto and A. Ogawa, *Chem. – Eur. J.*, 2019, **25**, 6797–6806.
20 V. A. Tzschach and S. Raensch, *J. Prakt. Chem.*, 1971, **313**, 254–258.
21 H. Kim, Z.-w Qu, S. Grimme, N. Al-Zuhaika and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2023, **62**, e202312587.
22 H. Kim and D. W. Stephan, *Dalton Trans.*, 2023, **52**, 5023–5027.
23 N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2003, **125**, 14404–14410.
24 N. Burford, T. S. Cameron and P. J. Ragogna, *J. Am.Chem. Soc.*, 2001, **123**, 7947–7948.
25 S. S. Chitnis, E. MacDonald, N. Burford, U. Werner-Zwanziger and R. McDonald, *Chem. Commun.*, 2012, **48**, 7359–7361.
26 K. L. Bamford, S. S. Chitnis, R. L. Stoddard, J. S. McIndoe and N. Burford, *Chem. Sci.*, 2016, **7**, 2544–2552.
27 N. Burford, D. E. Herbert, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2004, **126**, 17067–17073.
28 J. M. Slattery, C. Fish, M. Green, T. N. Hooper, J. C. Jeffery, R. J. Kilby, J. M. Lynam, J. E. McGrady, D. A. Pantazis, C. A. Russell and C. E. Willans, *Chem. – Eur. J.*, 2007, **13**, 6967–6974.
29 M. B. Abrams, B. L. Scott and R. T. Baker, *Organometallics*, 2000, **19**, 4944–4956.
30 O. Ekkert, G. Kehr, R. Fröhlich and G. Erker, *Chem. Commun.*, 2011, **47**, 10482–10484.
31 D. Gasperini, S. E. Neale, M. F. Mahon, S. A. Macgregor and R. L. Webster, *ACS Catal.*, 2021, **11**, 5452–5462.
32 D. C. R. Hockless, M. A. McDonald, M. Pabel and S. B. Wild, *Chem. Commun.*, 1995, 257–258.
33 D. C. R. Hockless, M. A. McDonald, M. Pabel and S. B. Wild, *J. Organomet. Chem.*, 1997, **529**, 189–196.
34 A. Ueno, J. Moricke, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2018, **54**, 13746–13749.
35 N. Al-Zuhaika, S. Severin, M. D. Schmuckler, A. J. Lough and D. W. Stephan, CCDC 2444558: Experimental Crystal Structure Determination, 2025, DOI: **10.5517/ccdc.csd.cc2n1rq6**.
36 N. Al-Zuhaika, S. Severin, M. D. Schmuckler, A. J. Lough and D. W. Stephan, CCDC 2444559: Experimental Crystal Structure Determination, 2025, DOI: **10.5517/ccdc.csd.cc2n1rr7**.
37 N. Al-Zuhaika, S. Severin, M. D. Schmuckler, A. J. Lough and D. W. Stephan, CCDC 2444560: Experimental Crystal Structure Determination, 2025, DOI: **10.5517/ccdc.csd.cc2n1rs8**.

