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From phosphaimines to phosphanes via transient iminozirconiophosphoranes

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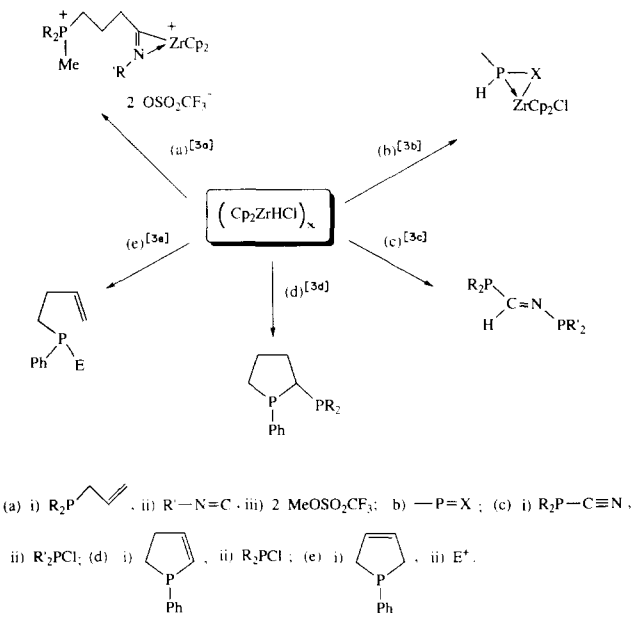
Abstract

Transient iminozirconiophosphoranes **3a–3c**, **8** and **13** can be generated from phosphaimines **2a–2c** and zirconocenes derivative [Cp_2ZrRR']. A plausible reaction mechanism involving transfers of various groups from phosphorus to zirconium is presented.

Keywords: Titanium; Zirconium; Phosphorimines; Iminozirconiophosphoranes; Phosphaimine; Amminophosphine

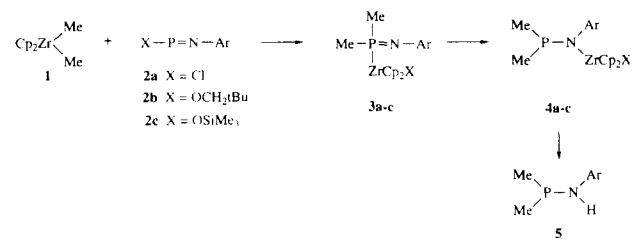
1. Introduction

It is only recently that interactions between compounds of Group 4 elements and Main Group elements have been intensively investigated. Reports of zirconocene compounds for the functionalization of phosphorus compounds are of particular interest, as in insertion of [Cp_2Zr] into the carbon–halogen bond of halophosphinines followed by addition of electrophiles [1], and in zirconium-assisted functionalizations of an unsaturated phosphorus–nitrogen–sulfur heterocycle with [Cp_2ZrCl_2] [2]. We have already reported how [Cp_2ZrHCl] can functionalize a great variety of unsaturated linear or cyclic phosphorus derivatives [3a–3e] (Scheme 1). Moreover, [Cp_2ZrMe_2] **1** was found to be an efficient reagent for the transformation of the halogenophosphaimine Cl–P=N–Ar **2a** (Ar = 2,4,6-$^{k}Bu_3C_6H_2$) into the phosphane Me_2PNHAr **5** via a relatively stable iminozirconiophosphorane [$Me_2P(ZrCp_2Cl)$=N–Ar] **3a**, which was to our knowledge the first *P*-metallated iminophosphorane reported [4] (Scheme 2). Compound **3a** was the kinetic product of the reaction and migration of the $ZrCp_2Cl$ moiety from phosphorus to nitrogen readily occurred at room temperature, affording the phosphane **4a**. The Zr–N bond of **4a** was cleaved easily in the presence of proton sources (solvent, traces of water) to give compound **5**.



(a) i) R_2P , ii) R'–N=C , iii) 2 $MeOSO_2CF_3$; b) —P=X ; (c) i) R_2P–C≡N , ii) R'_2PCl; (d) i) , ii) R_2PCl ; (e) i) , ii) E^+.

Scheme 1.



Scheme 2.

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We were therefore interested to see whether this type of reaction could be extended to other phosphaimines, or to other $[Cp_2ZrR_2]$.

Here we report the reaction of $[Cp_2ZrMe_2]$ **1** with phosphaimines R–P=N–Ar **2** (**b** R = $OCH_2{}^tBu$, **c** R = $OSiMe_3$, **d** R = OSO_2CF_3) as well as the reaction of chlorophosphaimine **2a** with $[Cp_2ZrR'_2]$ (R' = CH_2SiMe_3 or R' = CH_2Ph) or $[Cp_2Zr(Me)(OMe)]$. Evidence for the transient formation of various iminozirconiophosphoranes $[Me_2P(ZrCp_2X)=N-Ar]$ (X = R or OR) involving transfer of $OCH_2{}^tBu$, $OSiMe_3$, or OSO_2CF_3 groups from phosphorus to zirconium will be provided.

2. Results and discussion

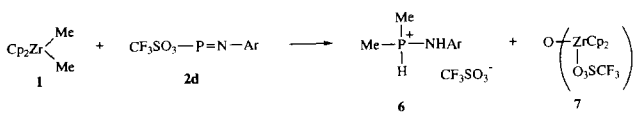
Addition of $[Cp_2ZrMe_2]$ **1** to an ethereal or THF solution of phosphaimine **2b** or **2c** at −78°C led to the phosphane **5** in excellent yield (greater than 80%) (Scheme 2). Reactions were monitored by ^{31}P NMR spectroscopy which showed the transient formation of a derivative with a $\delta\ ^{31}P$ of −5.5 (for the reaction of **2b** and **1**) or −3.5 (for the reaction of **2c** and **1**) ppm. These signals disappeared quickly even at low temperature and were replaced by a singlet in the range 32–80 ppm which, in turn, rapidly disappeared to give another singlet at 33.3 ppm, corresponding to the formation of **5**. Attempts to isolate these intermediates have failed. Nevertheless, based on our previous results [4] (Scheme 2) it seems reasonable to postulate that ^{31}P chemical shifts at −5.5 ppm or −3.5 ppm correspond to the unstable iminozirconiophosphoranes **3b,3c** whereas the ^{31}P chemical shifts at 32–80 ppm correspond to the *N*-zirconated phosphanes **4b,4c**. The ^{31}P NMR chemical shift of the iminozirconiophosphorane **3a** which was previously isolated and fully characterized was close to these values (**3** δ = −4.3) and the phosphane $[Me_2PN(ZrCp_2Cl)Ar]$ **4a** showed $\delta\ ^{31}P$ of 31.8.

A similar reaction of **1** and the phosphaimine **2d** gave rise to the protonated form of **3**, i.e. the phosphonium salt **6** and the zirconium oxide $[\{Cp_2Zr(OSO_2CF_3)\}_2O]$ **7** (Scheme 3).

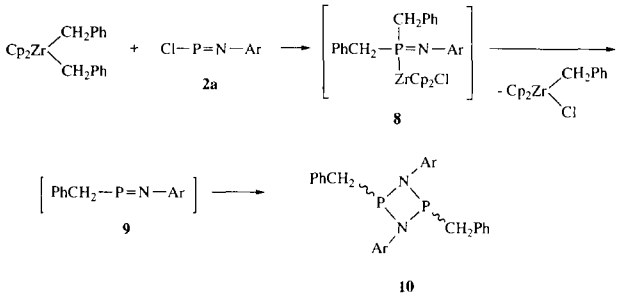
The unexpected phosphaimine-phosphane transformation reported here involves an easy transfer of alcoxy, trimethylsiloxy or triflate groups from phosphorus to zirconium with the transient formation of unstable *P*-metallated iminophosphoranes.

In order to study the effects of zirconium substituents on the course of the reaction we investigated the reactivity of **2a** with $[Cp_2Zr(CH_2SiMe_3)_2]$, $[Cp_2Zr(CH_2Ph)_2]$ and $[Cp_2Zr(Me)(OMe)]$. Probably because of the steric hindrance introduced by the CH_2SiMe_3 groups, no reaction occurred between **2a** and $[Cp_2Zr(CH_2SiMe_3)_2]$. A similar observation was made with the corresponding titanium derivative $[Cp_2Ti(CH_2SiMe_3)_2]$. However, treatment of **2a** with $[Cp_2Zr(CH_2Ph)_2]$ gave rise unexpectedly to a mixture of *trans* and *cis* diazadiphosphetidines **10** ($\delta\ ^{31}P$ = 127.1 and 48.2) in a 9/1 ratio. There is now a considerable body of evidence to show that the "high field" isomer of diazadiphosphetidines of the type $(RO-P-N-{}^tBu)_2$ have *cis* structures [5], but the situation is not so clear with the corresponding *P*-alkyl diazadiphosphetidines and therefore the structural assignment for the major diazadiphosphetidine requires additional experiments. The reaction leading to **10** seemed to proceed as above, with the transient formation of the iminozirconiophosphorane **8** ($\delta\ ^{31}P$ = −3.8) which underwent an intramolecular elimination of $[Cp_2Zr(Cl)(CH_2Ph)]$ with the generation of the transient phosphaimine **9**. Spontaneous dimerization of **9** led finally to **10** (Scheme 4). Nevertheless, **9** was not detected by ^{31}P NMR spectroscopy. Therefore we tried to prepare **9** by another route involving **2a** and $PhCH_2MgCl$. However, this reaction did not lead to **9** and only the phosphinophosphaimine species **12** was formed, isolated and fully characterized. It is reasonable to postulate that **12** came from the transient generation of **9** which reacted further with **2a** to give the chlorophosphane **11**. In the presence of $PhCH_2MgCl$, **11** was converted to **12** (Scheme 5).

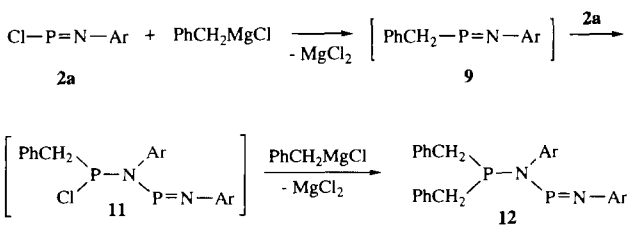
Lastly, we investigated the reaction of **2a** with $[Cp_2Zr(OMe)(Me)]$. Oxophilicity and halophilicity of zirconium should interfere here and might allow the



Scheme 3.



Scheme 4.



Scheme 5.

synthesis of other phosphanes. Indeed two phosphanes were formed, compound **5** and $(MeO)_2PNHAr$ **15** in a 1/1 ratio. It was possible to detect these by ^{31}P NMR spectroscopy. When the reaction was performed at −78°C, we observed not only signals from the intermediates **3a** and **4a**, but we also saw two other singlets at +2 ppm and +135.8 ppm attributed to the intermediates **13** and **14**, respectively (Scheme 6). Under the experimental conditions we used, $[Cp_2Zr(OMe)Me]$ should be in equilibrium with **1** and $[Cp_2Zr(OMe)_2]$ which react separately with chlorophosphaimine **2c**. Further experiments are underway to confirm this.

In conclusion, this work demonstrates additional examples of the transient formation of highly reactive *P*-metallated iminophosphoranes **3a–3c**, and **8**. It provides new types of interaction between Group 4 and Main Group element compounds. Efforts are now directed towards the full characterization of intermediates and the X-ray structure analysis of a stable $[R_2P(ZrCp_2R')=N-R']$ species.

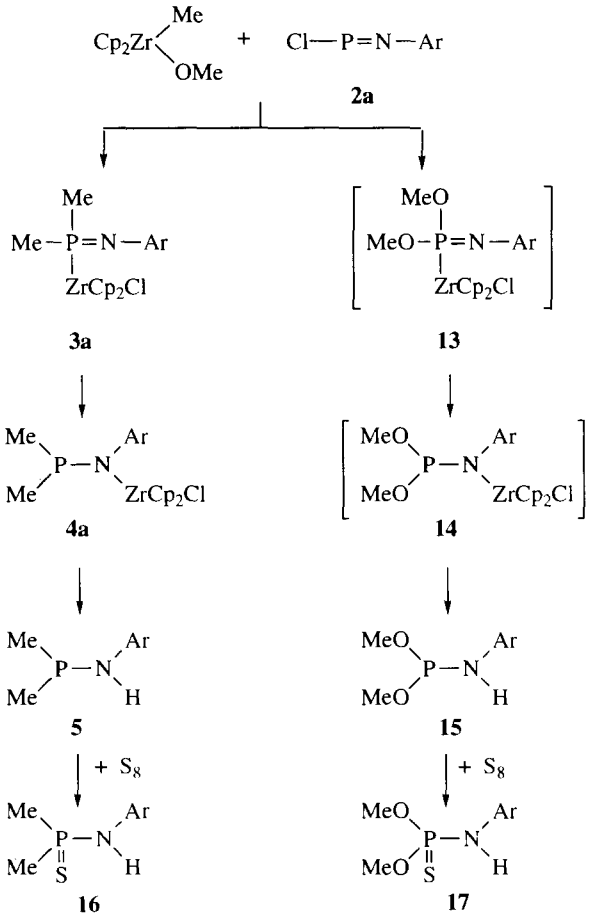
3. Experimental details

All manipulations were carried out with standard high vacuum or dry argon atmosphere techniques. NMR spectra were recorded at ambient temperature on 200- and 250-MHz Bruker spectrometers and referenced as follows. ^1H (δ) $CHDCl_2$ (5.32), C_6HD_5 (7.16); $^{13}C\{^1H\}$ (ppm) CD_2Cl_2 (53.8), C_6D_6 (128.0); $^{31}P\{^1H\}$ external 85% H_3PO_4 (0.0 ppm). Chemical shift are in δ (^1H) or ppm (^{13}C, ^{31}P), and coupling constants (J) are in Hertz. Mass spectra were obtained on a Nermag R10-10H. Microanalyses have been performed by the Centre de Microanalyse du CNRS or in our laboratories.

Solvents were purified as follows: THF and ether distilled from $Na/O=CPh_2$, CH_2Cl_2 distilled from P_2O_5, and pentane distilled from CaH_2. C_6D_6 and CD_2Cl_2, purchased from CEA, were treated with $LiAlH_4$, distilled, and stored under argon. $[Cp_2Zr(Me)R]$ (R = Me or OMe) [6], $[Cp_2Zr(CH_2Ph)_2]$ [7], $[Cp_2M(CH_2SiMe_3)_2]$ (M = Zr or Ti) [8], phosphaimines **2a** [9], **2b–2d** [10], were prepared by literature methods.

3.1. Synthesis of the aminophosphane 5

To a solution of phosphaimine RO–P=N–Ar (**2b** R = ^{t}BuCH$_2$, **2c** R = $SiMe_3$) (2.94 mmol) in THF (10 ml) at −78°C was added $[Cp_2ZrMe_2]$ (0.740 g, 2.94 mmol) dissolved in 10 ml of THF. The mixture was stirred for 30 min, the solvent evaporated of, and the



Scheme 6.

resulting white powder washed with pentane (2 × 20 ml) and dried under vacuum **5** [4] was obtained in 80–85% yield.

3.2. Synthesis of the phosphonium salt $[Me_2P(H)NHAr][CF_3SO_3]$ 6

To a solution of CF_3SO_3–P=N–Ar **2d** (0.123 g, 0.28 mmol) in ether (5 ml) was added dropwise at −78°C a solution of $[Cp_2ZrMe_2]$ (0.070 g, 0.28 mmol) in 10 ml of ether. The mixture was allowed to warm to room temperature. The precipitate formed during this reaction was isolated by filtration and was washed twice with 10 ml of pentane to give a white powder **6** (0.031 g, 0.10 mmol, 35% yield).

6: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.3. ^1H NMR ($CDCl_3$): δ 7.39 (s, 2H, CH_{Ar}), 7.32 (d, $^1J_{HP}$ = 521.2 Hz, 1H, HP), 5.82 (s, 1H, HN), 1.60 (d, $^2J_{HP}$ = 14.3 Hz, 6H, CH_3P), 1.39 (s, 18H, *o*-$C(CH_3)_3$), 1.23 (s, 9H, *p*-$C(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.5 (s, *p*-C_{Ar}), 134.2 (d, $^4J_{CP}$ = 5.0 Hz, *m*-C_{Ar}), 121.7 (d, $^3J_{CP}$ = 2.1 Hz, *o*-C_{Ar}), *i*-C_{Ar} not observed, 36.5 (s, *o*-CCH_3), 34.7 (s, *p*-CCH_3), 33.8 (s, *o*-CH_3), 30.3 (s, *p*-CCH_3), 7.8 (d, $^1J_{CP}$ = 68.1 Hz, CH_3P). MS *m/z*: 323 $[M + 1]^+$. Anal. calc. for $C_{20}H_{37}NP$: C, 74.53; H, 11.49. Found: C, 74.48; H, 11.44%.

3.3. Synthesis of diazadiphosphetidines 10

To a solution of chlorophosphaimine **2a** (0.325 g, 1.00 mmol) in THF (15 ml) was added dropwise at −78°C a solution of $[Cp_2Zr(CH_2Ph)_2]$(0.418 g, 1.00 mmol) in 10 ml of THF. The mixture was allowed to warm to room temperature. After evaporation of the solvent, the residue was washed with pentane (2 × 15 ml) to give an orange powder **10** (0.571 g, 0.75 mmol, 75% yield).

Major isomer: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 127.1 (s). ^1H NMR (C_6D_6): δ 7.49 (s, 10H, Ph), 7.01 (s, 4H, CH_{Ar}), 2.74 (s, 4H, CH_2), 1.55 (s, 36H, *o*-$C(CH_3)_3$), 1.37 (s, 18H, *p*-$C(CH_3)_3$).

Minor isomer: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 48.2 (s). ^1H NMR (C_6D_6): δ 7.49 (s, 10H, Ph), 7.01 (s, 4H, CH_{Ar}), 2.25 (s, 4H, CH_2), 1.39 (s, 36H, *o*-$C(CH_3)_3$), 1.25 (s, 18H, *p*-$C(CH_3)_3$).

MS *m/z*: 763 $[M + 1] +$. Anal. calc. for $C_{50}H_{72}P_2N_2$: C, 78.74; H, 9.45. Found: C, 78.66; H, 9.39%.

3.4. Synthesis of the phosphinophosphaimine 12

To a solution of chlorophosphaimine **2a** (0.450 g, 1.38 mmol) in THF (10 ml) was added at −78°C $PhCH_2MgCl$ (1.38 ml, 1.38 mmol). The mixture was allowed to warm to room temperature. After filtration and evaporation of the solvent from the filtrate pentane extraction (2 × 15 ml) gave **12** as a white powder (0.437 g, 0.60 mmol, 45% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 297.3 (d, $^2J_{PP}$ = 17.2 Hz, N–P=N), 96.8 (d, $^2J_{PP}$ = 17.2 Hz, C–P–N). ^1H NMR (C_6D_6): δ 7.69 (s, 2H, C_{Ar}), 7.66 (s, 2H, C_{Ar}), 7.43 (s, 5H, C_6H_5), 6.68 (s, 5H, C_6H_5), 4.04 (d, $^2J_{HP}$ = 13.6 Hz, 2H, CH_2), 3.28 (d, $^2J_{HP}$ = 13.5 Hz, 2H, CH_2), 1.80 (s, 18H, *o*-$C(CH_3)_3$), 1.64 (s, 18H, *o*-$C(CH_3)_3$), 1.45 (s, 9H, *p*-$C(CH_3)_3$), 1.33 (s, 9H, *p*-$C(CH_3)_3$). MS *m/z*: 763 $[M + 1]^+$. Anal. calc. for $C_{50}H_{72}P_2N_2$: C, 78.74; H, 9.45. Found: C, 78.62; H, 9.37%.

3.5. Reaction of chlorophosphaimine 2a with $[Cp_2Zr(OMe)(Me)]$

To a solution of **2a** (0.957 g, 2.94 mmol) in THF (10 ml) was added dropwise at −78°C a solution of $[Cp_2Zr(OMe)(Me)]$(0.786 g, 2.94 mmol) in 10 ml of THF. The mixture was allowed to warm to room temperature. After evaporation of the solvent the residue was washed with pentane (2 × 20 ml) to give a 1/1 mixture of phosphanes **5** and **15** Addition of sulfur to this mixture produced the corresponding sulfides $Me_2P(S)NHAr$ **16** and $(MeO)_2P(S)NHAr$ **17**, which were separated by column chromatography on silica gel (ether/pentane, 1:1) (**16** R_f: 0.56; **17** R_f: 0.84).

15: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 137.9. ^1H NMR: δ 7.57 (s, 2H, CH_{Ar}), 4.53 (d, $^2J_{HP}$ = 5.8 Hz, 1H, NH), 3.25 (d, $^3J_{HP}$ = 10.2 Hz, 6H, CH_3O), 1.63 (s, 18H, *o*-$C(CH_3)_3$), 1.32 (s, 9H, *p*-$C(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 151.8 (s, $^2J_{CP}$ = 4.0 Hz, *i*-C_{Ar}), 149.1 (d, $^3J_{CP}$ = 3.0 Hz, *o*-C_{Ar}), 146.9 (s, *p*-C_{Ar}), 123.7 (s, *m*-C_{Ar}), 50.2 (d, $^2J_{CP}$ = 10.6 Hz, CH_3O), 37.1 (s, *o*-CCH_3), 35.2 (s, *p*-CCH_3), 33.3 (s, *o*-CCH_3), 32.0 (s, *p*-CCH_3). MS *m/z*: 354 $[M + 1]^+$.

16: ^{31}P NMR (C_6D_6): δ 58.6. ^1H NMR (C_6D_6): δ 7.23 (s, 2H, CH_{Ar}), 3.71 (d, $^2J_{HP}$ = 5.38 Hz, 1H, NH), 1.56 (d, $^2J_{HP}$ = 12.8 Hz, 6H, CH_3P), 1.44 (s, 18H, *o*-$C(CH_3)_3$), 1.21 (s, 9H, *p*-$C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.5 (s, *p*-C_{Ar}), 147.4 (d, $^2J_{CP}$ = 3.4 Hz, *i*-C_{Ar}), 131.4 (d, $^3J_{CP}$ = 6.7 Hz, *o*-C_{Ar}), 123.4 (s, *m*-C_{Ar}), 36.9 (s, *o*-CCH_3), 34.3 (s, *p*-CCH_3), 33.2 (s, *o*-CCH_3), 31.2 (s, *p*-CCH_3), 23.3 (d, $^1J_{CP}$ = 70.9 Hz, CH_3P). MS *m/z*: 354 $[M + 1]^+$. Anal. calc. for $C_{20}H_{36}NPS$: C, 67.99; H, 10.20. Found: 67.86; H, 10.17%.

17: ^{31}P NMR (C_6D_6): δ 72.1. ^1H NMR (C_6D_6): δ 7.32 (s, 2H, CH_{Ar}), 4.55 (d, $^2J_{HP}$ = 10.2 Hz, 1H, NH), 3.61 (d, $^3J_{HP}$ = 13.5 Hz, 6H, CH_3OP), 1.48 (s, 18H, *o*-$C(CH_3)_3$), 1.28 (s, 9H, *p*-$C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 149.1 (s, *p*-C_{Ar}), 147.7 (s, *i*-C_{Ar}), 123.5 (d, $^4J_{CP}$ = 15.9 Hz, *m*-C_{Ar}), 121.9 (d, $^3J_{CP}$ = 15.2 Hz, *o*-C_{Ar}), 54.0 (d, $^2J_{CP}$ = 5.2 Hz, CH_3OP), 37.0 (s, *o*-CCH_3), 34.7 (s, *p*-CCH_3), 33.7 (s, *o*-CCH_3), 31.3 (s, *p*-CCH_3). Anal. calc. for $C_{20}H_{36}NO_2PS$: C 62.33; H 9.35. Found C, 62.26; H 9.27%. MS *m/z*: 386 $[M + 1]^+$.

Acknowledgment

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