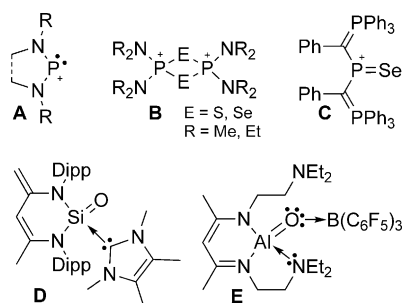


Lewis Base Stabilized Oxophosphonium Ions**

Arthur D. Hendsbee, Nick A. Giffin, Yaoting Zhang, Cory C. Pye, and Jason D. Masuda*

Dedicated to Professor Guy Bertrand on the occasion of his 60th birthday

The rich functional group chemistry of phosphorus has been exploited over the last several decades and even as of late, there have been major advances to the field.^[1] There have been regular contributions^[2–6] to the area of N-heterocyclic phosphonium ions **A** since the first reports 30 years ago.^[7,8] The area has seen a recent resurgence^[6,9–23] which may be due to the popularity of the isovalent singlet carbenes and, as such, the use of phosphonium ions as ligands in transition metal chemistry has been exploited.^[24–30] In the context of main group chemistry,^[31] phosphonium ions have been involved in the preparation of phosphinophosphonium systems,^[32–40] as well in reactions with P₄,^[39,41–44] and other reagents.^[15]

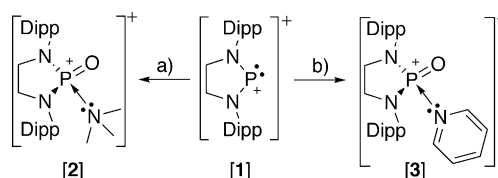


Approximately 20 years ago, the synthesis of terminal thio- and selenoxophosphonium ions were targeted by Burford et al.,^[45–47] however these attempts resulted in the formation of dimeric structures **B**. In 1992, Schmidpeter et al. reported a monomeric selenoxophosphonium ion **C**,^[48] which is resonance stabilized by flanking ylde substituents; unfortunately

no X-ray data was available to support the spectroscopic data. In a seminal review by Bertrand and Guerret,^[49] it was stated, “...so far, no oxophosphonium ions have been reported in the literature”. To the best of our knowledge, in the 15 years since the review, this feat has yet to be accomplished. Importantly, other monomeric compounds containing third-row elements and having E=O bonds have been recently reported, namely the Lewis acid or Lewis base (**D**) stabilized silanones^[50–52] and the Lewis acid and base stabilized aluminone **E**.^[53]

In these preliminary investigations, phosphonium ions are used as convenient starting materials for the preparation of oxophosphonium cations, which are stabilized by a Lewis base. These cations can be considered to be a phosphorus analogue of urea, where a phosphorus atom replaces the urea carbon. Electronic-structure calculations reveal the distribution of charge in the molecule and give credence to the fact this is indeed a phosphorus-based cation.

The addition of trimethylamine *N*-oxide to a dichloromethane solution of phosphorus salt **[1][GaCl₄]**^[54] resulted in formation of a yellow-colored solution, followed by precipitation of **[2][GaCl₄]** as an off-white solid (Scheme 1).



Scheme 1. Preparation of **[2][GaCl₄]** and **[3][X]** from **[1][X]**; Dipp = 2,6-diisopropylphenyl, **[X]** = **[GaCl₄]** or **[OTf]**; a) ONMe₃, CH₂Cl₂ (RT, 1 h); b) ONC₅H₅, CH₂Cl₂ (RT, 1 h).

³¹P NMR spectroscopic analysis revealed a single peak at δ = 26.0 ppm, which is significantly upfield of the peak corresponding to **1** (δ = 267.2 ppm). ¹H NMR spectroscopy revealed a symmetric structure overall with the peak corresponding to the trimethylamine fragment present at δ = 3.07 ppm and showing coupling to phosphorus (³J_{P-H} = 8.6 ppm). These data imply that insertion of the cationic P^{III} center into the nitrogen–oxygen bond may have occurred, thus resulting in oxidation of the phosphorus center to P^V with coordination of the Lewis basic NMe₃ to the cationic phosphorus center.

This hypothesis was confirmed by single-crystal X-ray crystallography (m.p. 256.8–257.0 °C; Figure 1).^[54] Indeed, analysis of crystals of **[2][GaCl₄]** grown from a concentrated CH₂Cl₂ solution revealed a tetrahedral phosphorus center attached to the bidentate ligand together with both a terminal

[*] A. D. Hendsbee, N. A. Giffin, Y. Zhang, Prof. Dr. C. C. Pye, Prof. Dr. J. D. Masuda
The Maritimes Centre for Green Chemistry and the Department of Chemistry, Saint Mary's University
Halifax, NS, B3H 3C3 (Canada)
E-mail: jason.masuda@smu.ca

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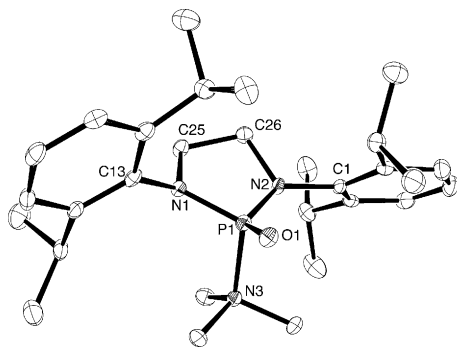


Figure 1. Solid-state structure of $[2]^+$ (hydrogen atoms and the $[\text{GaCl}_4]$ anion have been omitted for clarity). Ellipsoids are projected at 50% probability. Selected bond lengths [Å] and angles [°]: N1–P1 1.6306(18), N2–P1 1.6345(19), N3–P1 1.8431(19), O1–P1 1.4586(15), C25–N1 1.488(3), C25–C26 1.527(3), C26–N2 1.490(3); C13–N1–C25 119.36(17), C13–N1–P1 123.99(15), C25–N1–P1 111.58(14), C1–N2–C26 116.48(17), C1–N2–P1 129.53(15), C26–N2–P1 111.02(14), O1–P1–N1 119.61(9), O1–P1–N2 124.70(9), N1–P1–N2 97.50(9), O1–P1–N3 101.22(9), N1–P1–N3 107.09(9), N2–P1–N3 105.23(9).

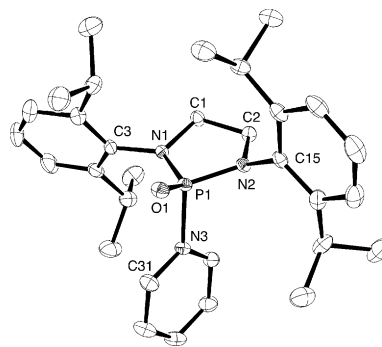


Figure 2. Solid-state structure of $[3]^+$ (hydrogen atoms and the $[\text{GaCl}_4]$ anion have been omitted for clarity). Ellipsoids are projected at 50% probability. Selected bond lengths [Å] and angles [°]: O1–P1 1.4594(14), P1–N2 1.6234(16), P1–N1 1.6257(16), P1–N3 1.8116(16), N1–C1 1.479(2), N2–C2 1.489(2); C3–N1–C1 119.18(15), C3–N1–P1 126.11(13), C1–N1–P1 113.52(12), C15–N2–C2 120.24(15), C15–N2–P1 122.62(13), C2–N2–P1 112.22(12), O1–P1–N2 120.28(8), O1–P1–N1 124.26(8), N2–P1–N1 97.40(8), O1–P1–N3 103.01(8), N2–P1–N3 107.05(8), N1–P1–N3 102.92(8).

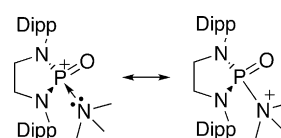
oxygen atom and trimethylamine coordinated to phosphorus. The phosphorus–oxygen bond (O1–P1 1.4586(15) Å) was found to be shorter than that in $\text{O}=\text{PPh}_3$ (1.491(2) Å),^[55] thus suggesting the cationic nature of the phosphorus center. The P–N distances in the heterocycle (N1–P1 1.6306(18) Å and N2–P1 1.6345(19) Å) are only slightly different to those of $[1][\text{GaCl}_4]$ (N1–P1 1.6103(14) Å and N2–P1 1.6128(14) Å). The P–N distance to the trimethylamine fragment is much longer (N3–P1 1.8431(19) Å), thus indicating the possible dative nature of the interaction between the nitrogen lone pair to the phosphorus cation. There are few examples in the literature to compare this P–N interaction with, the closest being $[4\text{-dimethylaminopyridine}-\text{PPh}_2]^+$, for which the pyridine N–P distance (1.789(1) Å) is shorter than that seen in $[2]^+$.^[56] It should be noted that there are no significant interactions between the phosphorus center and the $[\text{GaCl}_4]$ ion ($\text{P}\cdots\text{Cl}$ distance > 5 Å).

We attempted to exchange the NMe_3 in $[2][\text{GaCl}_4]$ with stronger Lewis bases such as pyridine or 4-dimethylaminopyridine and we did not observe any exchange in solution as determined by ^{31}P NMR spectroscopy.

To confirm that this reactivity can be extended to another *N*-oxide and is not dependant on the counter anion, we reacted both the tetrachlorogallate and triflate^[6,15] salts of $[1]^+$ with pyridine *N*-oxide. Salts $[3][\text{GaCl}_4]$ and $[3][\text{OTf}]$ were isolated as off-white powders in moderate yield. ^{31}P NMR spectroscopy revealed a single product was formed in both cases, with chemical shifts ($\delta = 12$ ppm) slightly upfield from those in the spectra of $[2][\text{GaCl}_4]$, thus indicating that a similar reaction might have occurred. This hypothesis was confirmed by single-crystal X-ray analysis. Both compounds $[3][\text{GaCl}_4]$ (m.p. 150 °C decomp.; Figure 2) and $[3][\text{OTf}]$ (m.p. 145.6–146.1 °C) crystallized from an evaporating dichloromethane solution.^[54] The structures once again reveal insertion of the phosphorus cation into the oxygen–nitrogen bond with no significant cation–anion interactions (closest P $\cdots$ O interaction for $[3][\text{OTf}]$ is > 4.9 Å; closest P $\cdots$ Cl interaction

for $[3][\text{GaCl}_4]$ is approximately 5.5 Å). As these are similar compounds, the discussion will be limited to the gallium salt. The length of phosphorus–oxygen bond (O1–P1 1.4594(14) Å) is statistically indistinguishable from that in $[2]^+$, whereas the pyridine nitrogen–phosphorus bond (P1–N3 1.8116(16) Å) is slightly shorter than that observed in $[2]^+$. This finding is most likely due to the better σ -donor ability of pyridine versus that of NMe_3 .

Determination of the location of the positive charge is important as there are two general resonance structures that can be drawn for these oxophosphonium systems (Scheme 2). One structure with the phosphorus atom bearing a positive charge (thus an oxophosphonium ion) and one with the amine/pyridine nitrogen bearing the positive charge (thus a P^{V} system with ammonium or pyridinium substituents).



Scheme 2. Two possible resonance structures: either a base-stabilized oxophosphonium cation (left) or a phosphine oxide with an ammonium substituent (right).

To assess the bonding situation in these oxophosphonium systems, a natural bond orbital (NBO) analysis of the bonding and atomic charges was performed. Structures of $[2]^+$ and $[3]^+$ as well as the Lewis base free oxophosphonium ion **F** were optimized at the B3PW91/6-311 + G(p) level of theory.^[57]

The NBO analysis reveals that the P–O bonds in both the NMe_3 - and pyridine-containing systems show sp^2 character and are strongly polarized towards oxygen (26% P and 74% O; 27% P and 73% O; respectively). Interestingly, the electron-donating Lewis base attached to the phosphorus

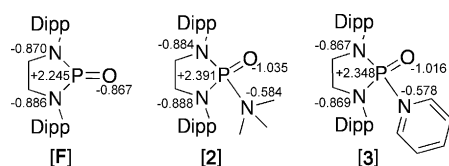
center appears to have little effect on the P=O bond; in the base-free system [F], NBO analysis again shows the P=O bond has sp^2 character and strong polarization towards oxygen (26% P and 74% O). The Wiberg bond indices (Table 1) show a P–O bond order of 1.54 in the base-free

Table 1: Wiberg bond indices for the base-free oxophosphonium cation [F]⁺ and the base-stabilized cations [2]⁺ and [3]⁺. Geometries are optimized at the B3PW91/6-311+G(d) level of theory.

	[F] (no Lewis base)	[2] (NMe ₃)	[3] (pyridine)
P=O	1.537	1.333	1.136
P–N _{het}	0.986	0.8384	0.816
P–N _{het}	0.986	0.8289	0.830
P–N _{donor}	n/a	0.500	0.464

N_{het} = nitrogen atoms of the N-heterocyclic phosphonium ion,
N_{donor} = nitrogen atom of the base.

cation; this bond order decreases by about 13% upon coordination of the base. The Wiberg P–N_{donor} bond order is only 0.46 (NMe₃) and 0.50 (pyridine) for the dative bond. This finding helps explain the long P–N_{donor} distances that were noted in the crystal structures. The NBO charges are distributed similarly throughout the three systems (Scheme 3). In the base-free example, the phosphorus atom



Scheme 3. NBO^[58] charges for the base-free oxophosphonium cation [F] and the base-stabilized cations [2] and [3]. Geometries optimized at the B3PW91/6-311+G(d) level of theory.

has a +2.245 charge with the oxygen bearing a –0.867 charge. Addition of the NMe₃ fragment causes little change in the overall charges, with the exception of the oxygen atom, which has a slight increase of negative charge to –1.035.

In conclusion, we have prepared the first terminal oxophosphonium ions by the addition of amine and pyridine N-oxides to N-heterocyclic phosphonium salts. We hope to use these results as a stepping-stone towards the isolation of monomeric, Lewis base free oxophosphonium ions. Investigations towards this goal and the use of other oxygen-containing sources for the formation of oxophosphonium ions are ongoing.

Experimental Section

All preparations were done under an atmosphere of dry, oxygen-free nitrogen in an mBraun Labmaster SP inert atmosphere glove box. Solvents were purified using a solvent purification system manufactured by Innovative Technology, and stored over molecular sieves. Elemental analysis was carried out at the Saint Mary's University

Center for Environmental Analysis and Remediation (CEAR) on a PerkinElmer 2400 Series II CHN Analyzer. Melting points were recorded on an Electrothermal MEL-Temp 3.0 using glass capillaries with samples prepared and sealed under inert conditions. Hyflo Super Cel (Celite) was purchased from Aldrich Chemical Company and dried for 24 h in an oven prior to use. Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried overnight at 140 °C under vacuum. 2-Chloro-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholidine was prepared according to an updated literature procedure^[15] of the original method.^[6] NMR spectra were recorded on a Bruker-Avance 300 MHz spectrometer. Trace amounts of protonated solvent were used as internal references for ¹H NMR spectra and referenced relative to tetramethylsilane. The deuterated solvent was used as an internal reference for ¹³C{¹H} NMR spectra (referenced relative to tetramethylsilane), ³¹P NMR spectra were referenced to external 85% H₃PO₄, and the ¹⁹F spectra were referenced to external F₃B·OEt₂.

Preparation of [1][GaCl₄]: A 100 mL flask was charged with 2-chloro-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholidine (2.17 g; 4.99 mmol) and GaCl₃ (878 mg; 4.99 mmol) in CH₂Cl₂ (40 mL). Immediate formation of a yellow solution was observed. The solution was left to stir for 1 h after which time an aliquot was taken for ³¹P NMR spectroscopic analysis, which showed full conversion to [1][GaCl₄]. The solution was evaporated to dryness under reduced pressure and the resulting pale yellow solid was dissolved in a minimal amount of dichloromethane. The solution was layered with pentane for crystallization. The material was isolated by decanting the mother liquor, washing the crystals with pentane and drying in vacuo to give yellow-colored, block-like crystals (2.11 g). Yield: 69%. m.p.: 147.6–147.9 °C; ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.50 (m, 6H, Ar–H), 4.63 (m, 4H, N–CH₂), 3.12 (sept, ³J_{H–H} = 6.8 Hz, 4H, CH–(CH₃)₃), 1.45 (d, ³J_{H–H} = 6.8 Hz, 6H, CH–CH₃), 1.34 ppm (d, ³J_{H–H} = 6.8 Hz, 6H, CH–CH₃); ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ = 146.45, 146.41, 132.68, 128.81, 128.68, 126.26, 60.23, 60.13, 30.30, 26.68, 26.65, 24.30 ppm; ³¹P{¹H} NMR (121.5 MHz, CD₂Cl₂): δ = 267.2 ppm (s). Elemental analysis calcd (%) for C₂₆H₃₈Cl₄GaN₂P: C 50.28, H 6.17, N 4.51; found: C 49.59, H 6.29, N 4.51.

Preparation of [2][GaCl₄]: A 20 mL scintillation vial was charged with [1][GaCl₄] (40 mg; 0.066 mmol) and CH₂Cl₂ (7 mL). This solution was then added to a solution of trimethylamine N-oxide (6.0 mg; 0.066 mmol) in CH₂Cl₂ (7 mL). Immediate formation of a yellow solution was observed, followed by the gradual formation of a precipitate and the loss of the yellow color. After 1 h of stirring, the solvent was removed under vacuum, residual solids were washed with a small amount of cold CH₂Cl₂ (<1 mL) to wash away residual [1][GaCl₄] and left to dry under vacuum to yield a tan-colored powder (38.2 mg, 0.0544 mmol). Yield: 83%. Suitable crystals for X-ray diffraction were grown by slow evaporation of a CH₂Cl₂ solution of [2][GaCl₄]. m.p.: 256.8–257.0 °C; ¹H NMR (300 MHz, CD₃CN): δ = 7.39–7.13 (m, 6H, Ar–H), 4.10 (m, 2H, N–CH₂), 3.81 (m, 2H, N–CH₂), 3.71 (sept, ³J_{H–H} = 6.8 Hz, 2H, CH–(CH₃)₃), 3.40 (sept, ³J_{H–H} = 6.8 Hz, 2H, CH–(CH₃)₃), 3.07 (d, ³J_{P–H} = 8.6 Hz, 9H, N–(CH₃)₃), 1.46 (d, ³J_{H–H} = 6.6 Hz, 12H, CH–CH₃), 1.28 (d, ³J_{H–H} = 6.6 Hz, 6H, CH–CH₃), 1.26 ppm (d, ³J_{H–H} = 6.8 Hz, 6H, CH–CH₃); ¹³C{¹H} NMR (75.4 MHz, CD₃CN): δ = 148.57, 148.50, 133.27, 130.8, 126.90, 126.54, 118.20, 51.91, 51.70, 51.54, 27.72, 26.90, 26.59, 23.85, 22.70 ppm; ³¹P NMR (121.5 MHz, CD₃CN): δ = 26.02 (dec ³J_{P–H} = 8.6 Hz). Elemental analysis calcd (%) for C₂₉H₄₇Cl₄GaN₃OP: C 50.03, H 6.80, N 6.04; found: C 49.86, H 6.63, N 5.99.

Preparation of [3][GaCl₄]: A 20 mL scintillation vial was charged with [1][GaCl₄] (250 mg; 0.403 mmol) and CH₂Cl₂ (9 mL). This solution was then added to a solution of pyridine N-oxide (38.3 mg; 0.403 mmol) in CH₂Cl₂ (9 mL). Immediate formation of a yellow solution was observed, followed by a change in color to a faint-pink-colored solution and formation of a precipitate. After 1 h of stirring, the solvent was removed under vacuum and [3][GaCl₄] (212 mg; 0.296 mmol) of was obtained as a tan-colored powder. Yield: 73.5%.

Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution containing **[3][GaCl₄]**. m.p: 150 °C (decomp.); ^1H NMR (300 MHz, CD_2Cl_2): δ = 9.48 (m, 2H, *ortho* C–H pyridine), 7.33 (m, 1H, *para* C–H pyridine), 8.32 (m, 2H, *meta* C–H pyridine), 7.44–7.36 (m, 4H, Ar–H), 7.15–7.13 (m, 2H, Ar–H), 4.43 (m, 2H, N–CH₂), 4.00 (m, 2H, N–CH₂), 3.67 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 2H, CH–(CH₃)₃), 2.86 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 2H, CH–(CH₃)₃), 1.51 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 6H, CH–CH₃), 1.40 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 6H, CH–CH₃), 1.29 (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 6H, CH–CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ = 149.56, 149.54, 149.38, 149.36, 149.26, 149.22, 145.94, 145.91, 130.62, 130.60, 129.92, 129.88, 129.01, 128.94, 126.69, 126.37, 125.69, 30.32, 29.740, 26.20, 24.60, 24.30 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 12.82 ppm (s). Elemental analysis calcd (%) for $\text{C}_{31}\text{H}_{45}\text{Cl}_4\text{GaN}_3\text{OP}$: C 51.99, H 6.05, N 5.87; found: C 51.08, H 6.06, N 5.85.

Preparation of **[3][OTf]**: A 20 mL scintillation vial was charged with **[1][OTf]** (250 mg, 0.449 mmol) and CH_2Cl_2 (9 mL). This solution was then added dropwise to a solution of pyridine *N*-oxide (42.7 mg; 0.449 mmol) in CH_2Cl_2 (9 mL). The solution was stirred for 1 h and then the solvent was removed under vacuum and **[3][OTf]** (220.6 mg; 0.338 mmol) was obtained as a tan-colored powder. Yield: 68.5%. Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution containing **[3][OTf]**. m.p: 145.6–146.1 °C, decomposition observed at 238 °C; ^1H NMR (300 MHz, CDCl_3): δ = 9.90 (m, 2H, *ortho* C–H pyridine), 8.60 (m, 1H, *para* C–H pyridine), 8.31 (m, 2H *meta* C–H pyridine), 7.35–7.28 (m, 4H, Ar), 7.07–7.04 (m, 2H, Ar–H), 4.67 (m, 2H, N–CH₂), 3.80 (m, 2H, N–CH₂), 3.68 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 2H, CH–(CH₃)₃), 3.01 (sept, $^3J_{\text{H-H}}$ = 6.8 Hz, 2H, CH–(CH₃)₃), 1.48 (d, $^3J_{\text{H-H}}$ = 6.7 Hz, 6H, CH–CH₃), 1.35 (d, $^3J_{\text{H-H}}$ = 7.4 Hz, 6H, CH–CH₃), 1.26 (d, $^3J_{\text{H-H}}$ = 6.5 Hz, 6H, CH–CH₃), 0.28 ppm (d, $^3J_{\text{H-H}}$ = 6.8 Hz, 6H, CH–CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.4 MHz, CDCl_3): δ = 149.58, 148.75, 147.77, 147.25, 129.82, 128.31, 126.97, 125.46, 125.140, 77.03, 76.59, 76.56, 49.44, 49.18, 28.71, 26.03, 24.96, 24.22, 23.54 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ = 12.55 ppm (s); ^{19}F NMR (282.3 MHz, CDCl_3): δ = –78.2 ppm (s). Elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{45}\text{F}_3\text{N}_3\text{O}_4\text{PS}$: C 58.79%, H 6.63, N 6.43; found: C 59.15, H 7.62, N 6.60.

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- [1] K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**.
- [2] N. Burford, P. Losier, P. K. Bakshi, T. S. Cameron, *J. Chem. Soc. Dalton Trans.* **1993**, 201–202.
- [3] N. Burford, P. Losier, C. Macdonald, V. Kyrimis, P. K. Bakshi, T. S. Cameron, *Inorg. Chem.* **1994**, 33, 1434–1439.
- [4] C. J. Carmalt, V. Lomeli, B. G. McBurnett, A. H. Cowley, *Chem. Commun.* **1997**, 2095–2096.
- [5] D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, *Chem. Eur. J.* **2000**, 6, 3414–3425.
- [6] M. B. Abrams, B. L. Scott, R. T. Baker, *Organometallics* **2000**, 19, 4944–4956.
- [7] S. Fleming, M. K. Lupton, K. Jekot, *Inorg. Chem.* **1972**, 11, 2534–2540.
- [8] B. E. Maryanoff, R. O. Hutchins, *J. Org. Chem.* **1972**, 37, 3475–3480.
- [9] B. D. Ellis, P. J. Ragogna, C. L. B. Macdonald, *Inorg. Chem.* **2004**, 43, 7857–7867.
- [10] G. Reeske, C. R. Hoberg, N. J. Hill, A. H. Cowley, *J. Am. Chem. Soc.* **2006**, 128, 2800–2801.

- [11] H. A. Spinney, G. P. A. Yap, I. Korobkov, G. DiLabio, D. S. Richeson, *Organometallics* **2006**, 25, 3541–3543.
- [12] D. Vidovic, Z. Lu, G. Reeske, J. A. Moore, A. H. Cowley, *Chem. Commun.* **2006**, 3501–3503.
- [13] B. D. Ellis, C. L. B. Macdonald, *Inorg. Chim. Acta* **2007**, 360, 329–344.
- [14] G. Reeske, C. R. Hoberg, A. H. Cowley, *Inorg. Chem.* **2007**, 46, 4358.
- [15] C. A. Caputo, J. T. Price, M. C. Jennings, R. McDonald, N. D. Jones, *Dalton Trans.* **2008**, 3461–3469.
- [16] J. W. Dube, G. J. Farrar, E. L. Norton, K. L. S. Szekely, B. F. T. Cooper, C. L. B. MacDonald, *Organometallics* **2009**, 28, 4377–4384.
- [17] A. B. Powell, J. R. Brown, K. V. Vasudevan, A. H. Cowley, *Dalton Trans.* **2009**, 2521–2527.
- [18] D. Gudat, *Top. Heterocycl. Chem.* **2010**, 21, 63–102.
- [19] A. L. Brazeau, C. A. Caputo, C. D. Martin, N. D. Jones, P. J. Ragogna, *Dalton Trans.* **2010**, 39, 11069–11073.
- [20] J. J. Weigand, K. Feldmann, F. D. Henne, *J. Am. Chem. Soc.* **2010**, 132, 16321–16323.
- [21] J. T. Price, M. Lui, N. D. Jones, P. J. Ragogna, *Inorg. Chem.* **2011**, 50, 12810–12817.
- [22] A. L. Brazeau, M. M. Hanninen, H. M. Tuononen, N. D. Jones, P. J. Ragogna, *J. Am. Chem. Soc.* **2012**, 134, 5398–5414.
- [23] A. L. Brazeau, N. D. Jones, P. J. Ragogna, *Dalton Trans.* **2012**, 41, 7890–7896.
- [24] H. A. Spinney, I. Korobkov, G. A. DiLabio, G. P. A. Yap, D. S. Richeson, *Organometallics* **2007**, 26, 4972–4982.
- [25] C. A. Caputo, M. C. Jennings, H. M. Tuononen, N. D. Jones, *Organometallics* **2009**, 28, 990–1000.
- [26] C. A. Caputo, A. L. Brazeau, Z. Hynes, J. T. Price, H. M. Tuononen, N. D. Jones, *Organometallics* **2009**, 28, 5261–5265.
- [27] B. Pan, M. W. Bezpalko, B. M. Foxman, C. M. Thomas, *Organometallics* **2011**, 30, 5560–5563.
- [28] G. S. Day, B. Pan, D. L. Kellenberger, B. M. Foxman, C. M. Thomas, *Chem. Commun.* **2011**, 47, 3634–3636.
- [29] B. Pan, Z. Xu, M. W. Bezpalko, B. M. Foxman, C. M. Thomas, *Inorg. Chem.* **2012**, 51, 4170–4179.
- [30] L. Rosenberg, *Coord. Chem. Rev.* **2012**, 256, 606–626.
- [31] N. Burford, P. J. Ragogna, *J. Chem. Soc. Dalton Trans.* **2002**, 4307–4315.
- [32] N. Burford, P. J. Ragogna, R. McDonald, M. J. Ferguson, *J. Am. Chem. Soc.* **2003**, 125, 14404–14410.
- [33] N. Burford, P. J. Ragogna, R. McDonald, M. J. Ferguson, *Chem. Commun.* **2003**, 2066–2067.
- [34] N. Burford, D. E. Herbert, P. J. Ragogna, R. McDonald, M. J. Ferguson, *J. Am. Chem. Soc.* **2004**, 126, 17067–17073.
- [35] N. Burford, C. A. Dyker, M. Lumsden, A. Decken, *Angew. Chem.* **2005**, 117, 6352–6355; *Angew. Chem. Int. Ed.* **2005**, 44, 6196–6199.
- [36] C. A. Dyker, N. Burford, M. D. Lumsden, A. Decken, *J. Am. Chem. Soc.* **2006**, 128, 9632–9633.
- [37] C. A. Dyker, S. D. Riegel, N. Burford, M. D. Lumsden, A. Decken, *J. Am. Chem. Soc.* **2007**, 129, 7464–7474.
- [38] C. A. Dyker, N. Burford, *Chem. Asian J.* **2008**, 3, 28–36.
- [39] J. J. Weigand, M. Holthausen, R. Frohlich, *Angew. Chem.* **2009**, 121, 301–304; *Angew. Chem. Int. Ed.* **2009**, 48, 295–298.
- [40] J. J. Weigand, N. Burford, R. J. Davidson, T. S. Cameron, P. Seelheim, *J. Am. Chem. Soc.* **2009**, 131, 17943–17953.
- [41] M. H. Holthausen, J. J. Weigand, *J. Am. Chem. Soc.* **2009**, 131, 14210–14211.
- [42] M. H. Holthausen, C. Richter, A. Hepp, J. J. Weigand, *Chem. Commun.* **2010**, 46, 6921–6923.
- [43] M. H. Holthausen, K. Feldmann, S. Schulz, A. Hepp, J. J. Weigand, *Inorg. Chem.* **2012**, 51, 3374–3387.
- [44] M. H. Holthausen, J. J. Weigand, *Z. Anorg. Allg. Chem.* **2012**, 638, 1103–1108.

- [45] N. Burford, R. E. v. H. Spence, R. D. Rogers, *J. Am. Chem. Soc.* **1989**, *111*, 5006–5008.
- [46] N. Burford, R. E. H. Spence, R. D. Rogers, *J. Chem. Soc. Dalton Trans.* **1990**, 3611–3619.
- [47] N. Burford, P. Losier, S. Mason, P. K. Bakshi, T. S. Cameron, *Inorg. Chem.* **1994**, *33*, 5613–5614.
- [48] A. Schmidpeter, G. Jochem, K. Karaghiosoff, C. Robl, *Angew. Chem.* **1992**, *104*, 1420–1421; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1350–1352.
- [49] O. Guerret, G. Bertrand, *Acc. Chem. Res.* **1997**, *30*, 486–493.
- [50] S. Yao, M. Brym, C. van Wuelen, M. Driess, *Angew. Chem.* **2007**, *119*, 4237–4240; *Angew. Chem. Int. Ed.* **2007**, *46*, 4159–4162.
- [51] Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7562–7563.
- [52] Y. Xiong, S. Yao, R. Mueller, M. Kaupp, M. Driess, *Nat. Chem.* **2010**, *2*, 577–580.
- [53] D. Neculai, H. W. Roesky, A. M. Neculai, J. Magull, B. Walfort, D. Stalke, *Angew. Chem.* **2002**, *114*, 4470–4472; *Angew. Chem. Int. Ed.* **2002**, *41*, 4294–4296.
- [54] CCDC 893764 ([1][GaCl₄]), 893761 ([2][GaCl₄]), 893763 ([3]-[GaCl₄]), and 893762 ([3][OTf]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [55] C. P. Brock, W. B. Schweizer, *J. Am. Chem. Soc.* **1985**, *107*, 6964–6970.
- [56] N. Burford, P. Losier, A. D. Phillips, P. J. Ragogna, T. S. Cameron, *Inorg. Chem.* **2003**, *42*, 1087–1091.
- [57] Structures were optimized using Gaussian03. See the Supporting Information for the full citation and xyz coordinates of the optimized structures. Comparison of the calculated structures and X-ray structures reveal nearly identical structures with only slight deviations in structural parameters.
- [58] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, *NBO 5.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2001**.