Ylide Ligands

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Bridging the Gap between Bisylides and Methandiides: Isolation, Reactivity, and Electronic Structure of an Yldiide**

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Abstract: *Bisylides and methandiides are two unique families of carbon bases that have found a variety of applications in recent years. Metalated ylides (yldiides) are the link between these types of compounds. Yet, only little is known about their properties, reactivities, and particularly their electronic structure. Here, we report the preparation of the metalated ylide* $[Ph_3P\text{-}C\text{-}SO_2Tol]^-$ *(**1**) with different alkali metal counterions. The compounds have been studied by X-ray diffraction analysis and NMR spectroscopy and the first structures of a sodium and potassium yldiide are presented. The electronic structure of **1** was explored by DFT calculations confirming its relation with other divalent carbon species. Reactivity studies demonstrate the strong nucleophilicity of the yldiide and its capability to act both as a σ- and π-donor.*

Since the first synthesis of an ylide more than a century ago[1] and their use in Wittig-type reactions[2] these compounds have been applied in a variety of important reactions, for example, for the synthesis of natural products and heterocycles.[3] In addition to their synthetic utility, their electronic structure has also been the subject of intensive research.[4] For a long time ylides have been described by two canonical structures—ylene (e.g. $R_3P{=}CR_2$) and ylide (e.g. $R_3P^+{-}C^-R_2$). While it has been shown that the contribution of the ylenic structure is minimal,[5] the description of ylides as phosphine-stabilized carbenes ($R_3P{\rightarrow}CR_2$) with a donor–acceptor interaction between phosphorus and carbon has found renewed interest.[6,7] Although ylide chemistry is now well-established, only very few reports have appeared on their metalated congeners, the so-called yldiides. Early studies by Corey revealed an enhanced reactivity in Wittig reactions with sterically hindered ketones[8] and Bestmann and co-workers demonstrated their potential in a series of multistep syntheses of alkynes and carbacycles.[9] The applicability of yldiides as ligands for transition metals has only been studied once by Chauvin and co-workers. Here, the yldiide was synthesized in the coordination sphere of the metal.[10] At present, only two yldiides have been isolated and structurally characterized: the silyl-substituted yldiide **A** synthesized by 1,2-addition of *n*-butyllithium to a carbene by the group of Bertrand[11] and phosphoranes **Ba/b** reported by Niecke (Figure 1 A).[12]

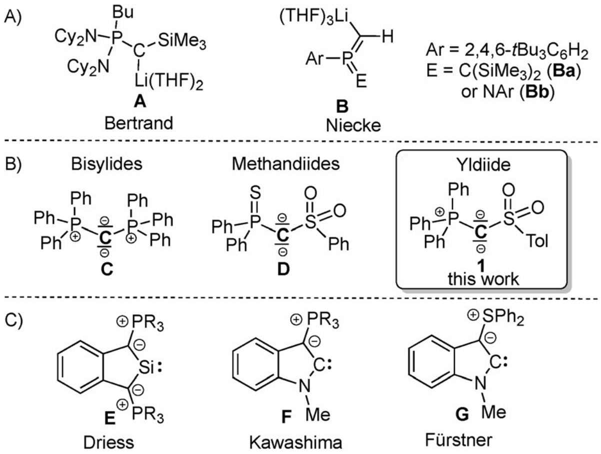

Figure 1. A) Isolated yldiides, B) structures of bisylides and methandiides, and C) ylide-stabilized divalent Group 14 compounds.

In a structural sense, yldiides can be viewed as the link between bisylides, such as carbodiphosphoranes (CDPs, for example, **C**),[13] and methandiides such as **D** (Figure 1 B).[14,15] Both have been shown to be very promising as carbon bases and ligands.[16] For example, CDP **C** is applicable in the activation and coordination of small molecules[17] such as CO_2, BH_3, and $GeCl_2$, and also as a ligand in transition metal complexes.[18] Despite the limited number of isolated yldiides, these compounds are likewise attractive as ligands. Owing to their structure they should exhibit unique σ- and π-donor abilities. This has been indicated by Driess, Kawashima, and Fürstner with the synthesis of ylide-stabilized silylene **E**[19] and carbenes **F** and **G** (Figure 1 C), respectively, although here no isolated yldiide ligand was used.[17c,20] For a general application of yldiides, however, the access of readily available and isolable representatives is necessary. Here we report the synthesis and isolation of $[Ph_3P\text{-}C\text{-}SO_2Tol]^-$ as such a readily accessible yldiide. We present the first structure elucidation of a sodium and potassium yldiide as well as the study of their electronic structure and reactivity, which confirms the capability of yldiides to act as σ- and π-donors.

In order to access an isolable yldiide, we aimed at the synthesis of the sulfonyl-substituted compound **1**. We assumed that the efficient coordination ability of the sulfonyl moiety towards alkali metals should support the stabilization

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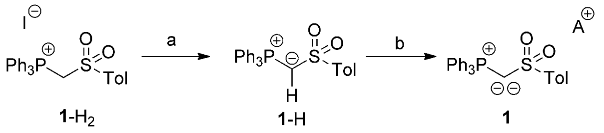


Scheme 1. Preparation of yldiide **1** from the phosphonium salt **1**-H_2 and ylide **1**-H; Tol = p-$C_6H_4CH_3$: a) nBuLi, −78 °C, THF or NaH, RT, THF; b) nBuLi, LiHMDS, NaHMDS, or KHMDS, THF or benzene, RT; A = Li, Na, or K.

of the metalated ylide and thus facilitate its isolation. The required phosphonium salt **1**-H_2 and the corresponding ylide **1**-H were prepared by modified literature procedures (Scheme 1, see the Supporting Information for experimental details).[21] Both compounds could be isolated in crystalline form and fully characterized by multinuclear NMR spectroscopy, elemental, and single-crystal X-ray diffraction analysis (Figure 2).[22] The second deprotonation to yldiide **1** was accomplished by using either a second equivalent of butyllithium or alternatively lithium, sodium, or potassium hexamethyldisilazide (LiHMDS, NaHMDS, KHMDS). The reaction was accompanied by a color change from colorless to yellow. $^{31}P\{^1H\}$ NMR spectroscopic studies showed quantitative deprotonation after only 1–6 h reaction time depending on the base used. Isolation of the product was found to be more convenient with NaHMDS and KHMDS due to the insolubility of the lithium compound in all common organic solvent. The sodium salt **1**-Na was thus obtained in 76 % yield by crystallization from benzene. **1**-K, on the other hand, could be isolated in 87 % yield in crystalline form after addition of 18-crown-6 or as an amorphous solid in 88 % yield after washing with hexane. When isolated, yldiide **1** was found to be stable in solution (benzene, toluene, THF) even at elevated temperatures and can be stored under an inert atmosphere for weeks.

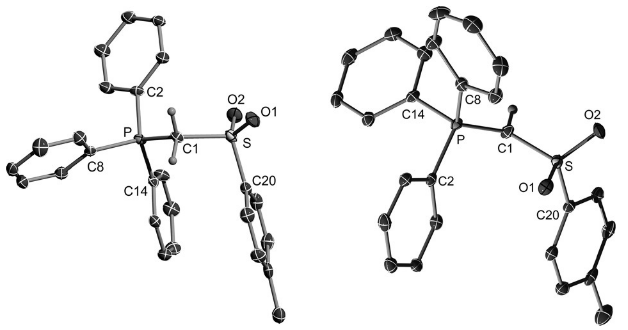


Figure 2. Molecular structures of the cation of phosphonium salt **1**-H_2 and ylide **1**-H. For selected bond lengths and angles, see Table 1. Displacement ellipsoids drawn at the 50 % probability level.

Yldiide **1** is characterized by the absence of the signal of any methylene proton and by an upfield shift in the $^{31}P\{^1H\}$ NMR spectrum from $\delta_P = 14.1$ ppm in **1**-H to $\delta_P = -12.1$ ppm for the potassium salt **1**-K and $\delta_P = -11.1$ ppm for the sodium compound **1**-Na. **1**-K features only broad signals in all NMR spectra recorded from C_6D_6 solution, thus indicating fluxional behavior in solution or the presence of different aggregates. Sharp signals, however, were observed for the 18-crown-6 adduct, suggesting the formation of one distinct species. The same holds true for the sodium salt **1**-Na in [D$_8$]THF. The metalated carbon atom gives rise to a broad signal at $\delta_C = 44.1$ ppm (**1**-K) and 41.2 ppm (**1**-Na), and is thus downfield-shifted relative to the analogous carbon atom im ylide **1**-H ($\delta_C = 34.5$ ppm).

Single crystals of $[Ph_3P\text{-}C\text{-}SO_2Tol]^-$ (**1**) could be obtained from THF solutions of the sodium and potassium salt, respectively. The latter required the use of one equivalent of 18-crown-6 for complexation of the metal. Both molecular structures (triclinic space group $P\bar{1}$) confirm the metalation of the central carbon atom (Figure 3). The sodium compound forms a C_i-symmetrical dimer, with three yldiides in the asymmetric unit. The central structural motif consists of two face-connected $(NaO)_4$ cubes, in which the Na ions form contacts with the ylidic carbon atoms (C1) and the oxygen atoms of the sulfonyl moieties. [**1**][K·18-crown-6] forms a monomeric structure. Here, the potassium ion is coordinated by the crown ether as well as by the metalated carbon atom and one oxygen atom of the sulfonyl moiety. The coordination of the yldiide results in an unsymmetrical complexation of the crown ether with the K–O bond lengths ranging between 2.790(1) and 3.022(1) Å. The K–C1 bond

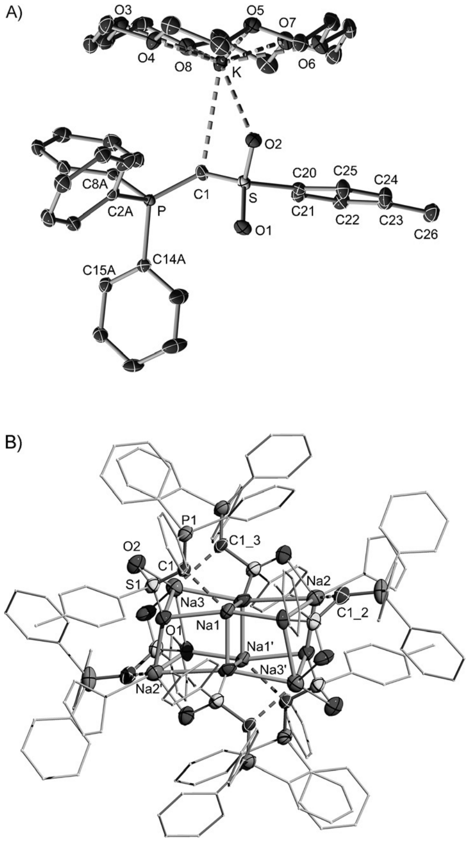


Figure 3. Molecular structures of [**1**][K·18-crown-6] (A) and $\{[\mathbf{1}]_3Na_3{\cdot}THF\}_2$ (B). Non-coordinating THF molecules and hydrogen atoms omitted for clarity. Displacement ellipsoids drawn at the 50 % probability level.

length of 3.154(2) Å is in the range of other organopotassium compounds.[23]

The most interesting features of the molecular structures of **1** concern the P-C-S linkage. Due to the higher quality of the data obtained for the potassium salt, those bond lengths and angles are only discussed here. However, analogous observations were made for the sodium compound (see the Supporting Information). The P-C-S linkage undergoes a dramatic contraction upon metalation (Table 1). A continuous bond shortening is thus observed in the series from **1**-H_2 to **1**-H and **1**. As such, the P–C1 and the S–C1 distances decrease from 1.808(3) Å and 1.809(3) Å in the phosphonium salt to 1.646(2) Å and 1.626(2) Å, respectively, in **1**. This shortening is due to electrostatic interactions within the P-C-S moiety upon metalation and the increase of the negative charge at the ylidic carbon atom. This is reflected by the NBO charges q_C at the central carbon atom. Additional negative hyperconjugation effects in **1**-H and **1** result in a lengthening of the S–O and P/S–C_{Ph} bonds (Table 1). The P-C-S angle also increases upon deprotonation, thus indicating a change in hybridization from sp^3 to sp^2.

Table 1: Experimental and calculated [values in brackets; M062X/6-311+g(d)] bond lengths [Å] and angles [°], calculated NBO charges, and NMR spectroscopic data of yldiide [**1**][K·18-crown-6] (C_6D_6), **1**-H, and [**1**-H_2][I] (CD_2Cl_2).

	1-H_2	**1**-H	**1**
P-C1	1.808(3) [1.833]	1.700(3) [1.699]	1.646(2) [1.650]
S-C1	1.809(3) [1.827]	1.683(3) [1.703]	1.626(2) [1.660]
P-C_{Ph}[a]	1.792(3) [1.800]	1.804(3) [1.823]	1.835(3) [1.850]
S-C_{Ph}	1.759(3) [1.775]	1.776(3) [1.799]	1.801(2) [1.822]
S-O[a]	1.441(2) [1.453]	1.446(2) [1.465]	1.478(1) [1.484]
P-C1-S	115.9(2) [118.6]	124.2(2) [119.9]	124.3(1) [118.1]
δ_H,$^2J_{PH}$ [ppm, Hz]	6.19, 12.4	2.93, 13.9	–
δ_C,$^1J_{PC}$ [ppm, Hz]	51.3, 45.9	34.5, 123.0	44.1 (br)[b] 41.2, 38.0[c]
q_C (calcd)	−0.95	−1.05	−1.33

[a] Average values. [b] For **1**-K. [c] For the sodium compound **1**-Na in [D_8]THF.

The utility of bisylides and methandiides is strongly connected to their basicity and the two pairs of electrons at the central carbon atom. To gain insight into the electronic structure of yldiides, density functional theory calculations [M062X/6-311+g(d)] on [Ph_3P-C-SO_2Tol]$^-$ (**1**) as well as on the related CDP **C** and methandiide **D** were performed (for computational details see the Supporting Information).

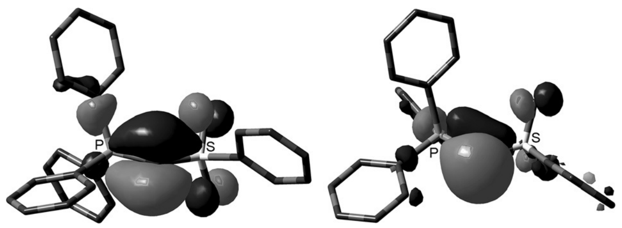
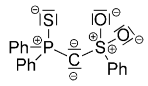
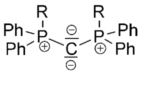
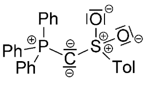


Figure 4. Kohn–Sham orbitals of **1** (HOMO (left) and HOMO−1 (right); isosurface values at 0.035 [M062X/6-311+g(d)].

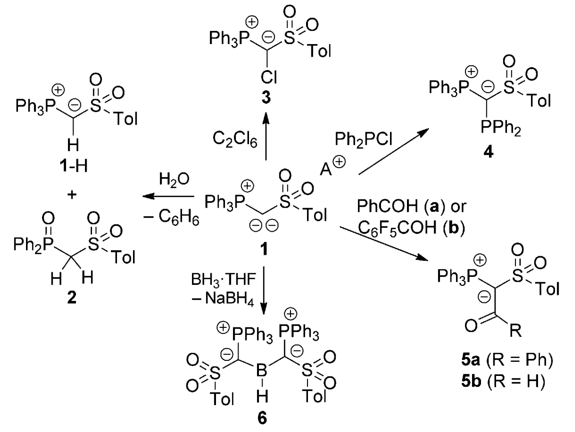
Figure 4 displays the two highest occupied molecular orbitals (HOMOs) of **1**. Both orbitals represent lone pairs of electrons at the central carbon atom, one of π- (HOMO) and one of σ-symmetry (HOMO−1). This is also reflected by the natural bond orbital (NBO) analysis of **1**, which showed two lone pair orbitals at the central carbon atom and two P/S–C σ-bonding orbitals (Table 2). This electronic structure is not only obtained for the "free" anion [Ph_3P-C-SO_2Tol]$^-$, but also for its sodium and potassium salts **1**-Na and **1**-K, which account for the additional metal–carbon interaction. Due to the predominantly ionic nature of the C–M bond, the metal ion has only a small influence on the overall electronic structure of the yldiide. It is interesting to note that despite the anionic nature of the methandiide and yldiide, the highest negative atomic partial charge at the central carbon atom (q_C) is found for the neutral CDP.[24] This can be attributed to the strong anion-stabilizing ability of the substituents in **1** and **D**. The calculated gas-phase proton affinities (PA) rank the basicity of **1** between those found for CDP **C** and methandiide **D**. Both the first and second PAs are higher than those of the corresponding CDP and lower than those of the methandiide, thus suggesting an intermediate reactivity.

Table 2: Results of the NBO analysis and proton affinities (PA) of CDP **C**, methandiide **D**, and yldiide **1** [energies in kcal mol^{-1}; M062X/6-311+g(d)].

	 **D**	 **C**	 **1**
*q*C	−1.40	−1.50	−1.33
*q*P	1.35	1.60	1.52
WBI C–P	1.30	1.34	1.42
P–C [Å]	1.668	1.647[a]	1.650
P-C-P/S [°]	124.7	127.7[a]	118.1
sp(C_{CP})/(%C)	$sp^{1.79}$ (56.8)	$sp^{1.70}$ (58.0)	$sp^{2.12}$ (55.1)
sp(C_{LP1})/(Occ.)	$sp^{1.92}$ (1.70)	$sp^{2.89}$ (1.64)	$sp^{1.43}$ (1.70)
sp(C_{LP2})/(Occ.)	p (1.52)	p (1.55)	p (1.51)
1st PA	429.4	274.1	351.7
2nd PA	325.9	179.2	247.2

[a] Experimentally determined P–C bond length (1.635(5) Å) and P-C-P angle (131.7(3)°).

Preliminary reactivity studies were performed to experimentally evaluate the nucleophilicity and coordination ability of yldiide **1** (Scheme 2, for details see the Supporting Information). As suggested by the high negative charge at the central carbon atom, the proton affinities, and frontier orbitals, [Ph_3P-C-SO_2Tol]$^-$ should be able to act as a strong σ- and π-donor. The nucleophilicity of **1** is demonstrated by its reactivity towards water to afford ylide **1**-H. Interestingly, this protonation reaction is accompanied by the formation of phosphine oxide **2**. This behavior is analogous to that observed for CDP **C**.[25] This nucleophilicity of **1** can also be used for the preparation of functionalized ylides. As such, treatment of **1** with one equivalent of hexachloroethane selectively provides the chlorinated ylide **3**, which could be isolated as a colorless, air and moisture-stable solid in 69%



Scheme 2. Reactivity studies of yldiide **1**.

yield. Likewise, reaction with diphenylchlorophosphine afforded the phosphanyl-substituted ylide **4** in 48% yield as a crystalline solid. The unique reactivity of the yldiide in comparison to simple ylides becomes evident from the reaction with benzaldehyde. Instead of the clean formation of the Wittig product, ketone **5** turned out to be the main product of the reaction and was isolated in 44% yield. This acylation formally arises from the elimination of sodium hydride from the alcoholate intermediate formed in the first reaction step.[26] The hydridic character and the reducing nature of this alcoholate can be attributed to the additional π-donor ability of the ylidiide ligand. This results in preferential hydride elimination over the formation of the Wittig product, which was only formed in small amounts (see the Supporting Information). The same reactivity is observed with pentafluorobenzaldehyde. However, in this case the C_6F_5 moiety acts as leaving group in a remarkably facile C−C bond-cleavage reaction.[27] This results in the formation of formylphosphorane **5b**, which was isolated in 62% yield.

The unique donor capacity of the yldiide ligand is also evident in the reaction of **1**-Na with $BH_3 \cdot THF$. Instead of formation of the corresponding sodium borate, selective formation of borane **6** and sodium borohydride is observed. Thus, for complete conversion to **6** a 2:3 yldiide/borane ratio has to be employed. Borane **6** was isolated in 78% yield and characterized by various spectroscopic methods. Most interestingly, X-ray crystallography revealed that **6** is a rare example of a monomeric organoborane.[28] In the molecular structure (Figure 5), **6** features a planar three-coordinate boron atom. The two ylide units are twisted with respect to each other, with slightly different B−C bond lengths of 1.513(4) and 1.528(4) Å. The monomeric nature can be attributed—at least in part—to the π-donation of the ylide ligand. This is confirmed by DFT studies of an energy-optimized model system of **6** (Me instead of Ph groups). The LUMO and HOMO−1 thus represent the π-bonding interactions between the ylide ligands and the borane moiety, which compensate for the Lewis acidity of boron. Due to the twisted arrangement of the ylide units, no symmetrical π-delocalization within the C-B-C linkage is observed and thus there are different B−C bond lengths in the crystal.

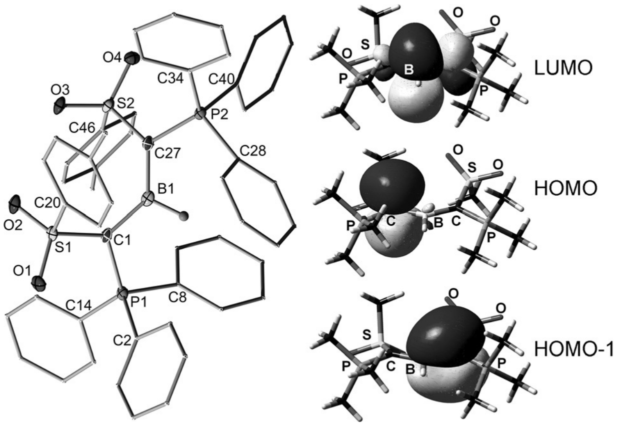


Figure 5. Molecular structure (left) and Kohn–Sham orbitals (right) of the ylide-stabilized borane **6**. Displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: C1–B 1.528(4), C27–B1 1.513(4), P1–C1 1.731(2), P2–C27 1.743(2), S1–C1 1.711(2), S2–C27 1.709(2); C27-B1-C1 131.9(2), S1-C1-P1 113.9(1), S2-C27-P2 112.6(1).

In summary, we have successfully synthesized and characterized the sulfonyl-stabilized metalated phosphorus ylide $[Ph_3P\text{-}C\text{-}SO_2Tol]^-$ (**1**). Employment of various metalating agents allowed the preparation of its different alkali metal salts and the first structure elucidation of a sodium and potassium yldiide. DFT studies confirmed the presence of two lone pairs of electrons at the central carbon atom and the strong basicity of the compound. Reactivity studies proved the unique donor capacity of the yldiide and its capability to act as both a σ- and π-donor. Hence, it represents a link between bisylides and methandiides. Given their applicability in main-group element and transition metal chemistry, further applications of metalated ylides as unique carbon bases can be expected.

Keywords: alkali metals · carbanions · lithium · structure elucidation · ylides

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[1] A. Michaelis, H. V. Gimborn, *Chem. Ber.* **1894**, *27*, 272.
[2] H. Staudinger, J. Meyer, *Helv. Chim. Acta* **1919**, *2*, 619.
[3] X. Huang, B. Peng, M. Luparia, L. F. R. Gomes, L. F. Veiros, N. Maulide, *Angew. Chem. Int. Ed.* **2012**, *51*, 8886.
[4] H. J. Bestmann, A. J. Kos, K. Witzgall, P. R. Schleyer, *Chem. Ber.* **1986**, *119*, 1331.
[5] H. Lischka, *J. Am. Chem. Soc.* **1977**, *99*, 353.
[6] a) H. Schmidbaur, *Angew. Chem. Int. Ed.* **1983**, *22*, 907; b) D. Seyferth, S. O. Grim, T. O. Read, *J. Am. Chem. Soc.* **1960**, *82*, 1510.
[7] For bisylides: R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem.* **2006**, *118*, 8206; b) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260; c) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273; d) D. Himmel, I. Krossing, A. Schnepf, *Angew. Chem.* **2014**, *126*, 378; e) H. Schmidbaur, *Angew. Chem. Int. Ed.* **2007**, *46*, 2984; f) G. Frenking, *Angew. Chem. Int. Ed.* **2014**, *53*, 6040.
[8] a) E. J. Corey, J. Kang, *J. Am. Chem. Soc.* **1982**, *104*, 4724; b) E. J. Corey, J. Kang, K. Kyler, *Tetrahedron Lett.* **1985**, *26*, 555.

[9] H. J. Bestmann, M. Schmidt, *Angew. Chem. Int. Ed.* **1987**, *26*, 79.

[10] R. Zurawinski, C. Lepetit, Y. Canac, R. Chauvin, *Inorg. Chem.* **2009**, *48*, 2147.

[11] S. Goumri-Magnet, H. Gornitzka, A. Baceiredo, G. Bertrand, *Angew. Chem. Int. Ed.* **1999**, *38*, 678.

[12] T. Baumgartner, B. Schinkels, D. Gudat, M. Nieger, E. Niecke, *J. Am. Chem. Soc.* **1997**, *119*, 12410.

[13] a) N. Dellus, T. Kato, N. Saffon-Merceron, V. Branchadell, A. Baceiredo, *Inorg. Chem.* **2011**, *50*, 7949; b) S. Pascual, M. Asay, O. Illa, T. Kato, G. Bertrand, N. Saffon-Merceron, V. Branchadell, A. Baceiredo, *Angew. Chem.* **2007**, *119*, 9236; *Angew. Chem. Int. Ed.* **2007**, *46*, 9078; c) T. Fujii, T. Ikeda, T. Mikami, T. Suzuki, T. Yoshimura, *Angew. Chem.* **2002**, *114*, 2688; *Angew. Chem. Int. Ed.* **2002**, *41*, 2576; d) F. Ramirez, N. B. Desai, B. Hansen, N. McKelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539; e) M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295.

[14] a) A. Kasani, R. P. K. Babu, R. McDonald, R. G. Cavell, *Angew. Chem.* **1999**, *111*, 1580; *Angew. Chem. Int. Ed.* **1999**, *38*, 1483; b) T. Cantat, L. Ricard, P. Le Floch, N. Mézailles, *Organometallics* **2006**, *25*, 4965; c) L. Orzechowski, G. Jansen, S. Harder, *Angew. Chem.* **2009**, *121*, 3883; *Angew. Chem. Int. Ed.* **2009**, *48*, 3825; d) H. Heuclin, M. Fustier-Boutignon, S. Y.-F. Ho, X.-F. Le Goff, S. Carenco, C.-W. So, N. Mézailles, *Organometallics* **2013**, *32*, 498; e) C. M. Ong, D. W. Stephan, *J. Am. Chem. Soc.* **1999**, *121*, 2939.

[15] a) J. Becker, V. H. Gessner, *Organometallics* **2014**, *33*, 1310; b) V. H. Gessner, F. Meier, D. Uhrich, M. Kaupp, *Chem. Eur. J.* **2013**, *19*, 16729; c) J. Becker, T. Modl, V. H. Gessner, *Chem. Eur. J.* **2014**, *20*, 11295; d) P. Schröter, V. H. Gessner, *Chem. Eur. J.* **2012**, *18*, 11223; e) K.-S. Feichtner, V. H. Gessner, *Dalton Trans.* **2014**, *43*, 14399.

[16] For examples, see: a) O. J. Cooper, D. P. Mills, J. McMaster, F. Moro, E. S. Davies, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem. Int. Ed.* **2011**, *50*, 2383; b) R. G. Cavell, R. P. K. Babu, A. Kasani, R. McDonald, *J. Am. Chem. Soc.* **1999**, *121*, 5805; c) T. Cantat, L. Ricard, N. Mézailles, P. Le Floch, *Organometallics* **2006**, *25*, 6030; d) G. Lin, N. D. Jones, R. A. Gossage, R. McDonald, R. G. Cavell, *Angew. Chem. Int. Ed.* **2003**, *42*, 4054; e) T. Cantat, T. Arliguie, A. Noël, P. Thuéry, M. Ephritikhine, P. Le Floch, N. Mézailles, *J. Am. Chem. Soc.* **2009**, *131*, 963.

[17] For examples, see: a) S. Khan, G. Gopakumar, W. Thiel, M. Alcarazo, *Angew. Chem. Int. Ed.* **2013**, *52*, 5644; b) M. Q. Yi Tay, Y. Lu, R. Ganguly, D. Vidovic, *Angew. Chem. Int. Ed.* **2013**, *52*, 3132; c) A. Fürstner, M. Alcarazo, K. Radkowski, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2008**, *47*, 8302–8306; d) M. Alcarazo, *Dalton Trans.* **2011**, *40*, 1839; e) W. Petz, F. Öxler, B. Neumüller, R. Tonner, G. Frenking, *Eur. J. Inorg. Chem.* **2009**, 4507.

[18] a) W. Petz, F. Weller, J. Uddin, G. Frenking, *Organometallics* **1999**, *18*, 619; b) J. Sundermeyer, K. Weber, *Organometallics* **1994**, *13*, 2560; c) M. Alcarazo, K. Radkowski, G. Mehler, R. Goddard, A. Fürstner, *Chem. Commun.* **2013**, *49*, 3140.

[19] M. Asay, S. Inoue, M. Driess, *Angew. Chem. Int. Ed.* **2011**, *50*, 9589; *Angew. Chem.* **2011**, *123*, 9763.

[20] S.-y. Nakafuji, J. Kobayashi, T. Kawashima, *Angew. Chem. Int. Ed.* **2008**, *47*, 1141; *Angew. Chem.* **2008**, *120*, 1157.

[21] a) J. Vicente, A. R. Singhal, *Organometallics* **2002**, *21*, 5887.

[22] The molecular structure of ylide **1-H** was already determined by Wheatley in 1965. P. J. Wheatley, *J. Chem. Soc.* **1965**, 5785.

[23] For examples, see: a) Y. Liu, T. C. Stringfellow, D. Ballweg, I. A. Guzei, R. West, *J. Am. Chem. Soc.* **2002**, *124*, 49; b) H. Schumann, D. M. M. Freckmann, S. Dechert, *Organometallics* **2006**, *25*, 2696; c) B. Conway, D. V. Graham, E. Hevia, A. R. Kennedy, J. Klett, R. E. Mulvey, *Chem. Commun.* **2008**, 2638; d) W. Clegg, B. Conway, D. V. Graham, E. Hevia, A. R. Kennedy, R. E. Mulvey, L. Russo, D. S. Wright, *Chem. Eur. J.* **2009**, *15*, 7074; e) N. D. R. Barnett, W. Clegg, A. R. Kennedy, R. E. Mulvey, S. Weatherstone, *Chem. Commun.* **2005**, 375.

[24] When M–C interactions are included in the calculations of **D** ($q_C = 1.49$) and **1** ($q_C = 1.41$ for **1**-K), the charges at carbon increase.

[25] W. Petz, F. Öxler, K. Aicher, B. Neumüller, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1751.

[26] The reducing nature of the intermediate alcoholate results in the reduction of benzaldehyde to benzyl alcohol. Thus 2 equiv of benzaldehyde must be used. The reaction is accompanied by the formation of considerable amounts of **1**-H, thus limiting the conversion to **5**. Note, that this reactivity is in contrast to that observed by Corey and co-workers with an in situ generated yldiide (Ref. [8]).

[27] Only few other examples exist in which $C_6F_5^-$ acts as a good leaving group. For examples, see: a) C. M. Garner, H. C. Fisher, *Tetrahedron Lett.* **2006**, *47*, 7405; b) T. Gerfaud, H.-L. Wei, L. Neuville, J. Zhu, *Org. Lett.* **2011**, *13*, 6172.

[28] a) M. Scheibitz, J. W. Bats, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2004**, *23*, 940; b) R. A. Bartlett, H. V. R. Dias, M. M. Olmstead, P. P. Power, K. J. Weese, *Organometallics* **1990**, *9*, 146; c) W.-C. Chen, C.-Y. Lee, B.-C. Lin, Y.-C. Hsu, J.-S. Shen, C.-P. Hsu, G. P. A. Yap, T.-G. Ong, *J. Am. Chem. Soc.* **2014**, *136*, 914.

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