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Reactions of Electrophiles with the Phosphaalkene Mes*P=CH$_2$: Mechanistic Studies of a Catalytic Intramolecular C−H Bond Activation Reaction

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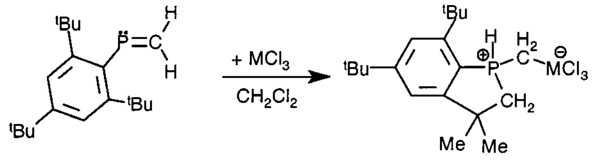
*Summary: A catalytic intramolecular C−H bond activation is reported for the reaction of the phosphaalkene Mes*P=CH$_2$ (Mes* = 2,4,6-tri-tert-butylphenyl) with aluminum(III) chloride (0.05, 0.10, and 0.15 equiv). Studies of analogous reactions with gallium(III) chloride and triflic acid facilitated the identification of intermediates, thus providing insight into the reaction mechanism, which involves a phosphenium ion as a fleeting intermediate.*

There is widespread interest in the study of compounds possessing (p−p)π bonds involving the heavier p-block elements and their analogy to C=C bonds.[1] Of particular interest to us is the preparation of new inorganic polymers by addition polymerization of heavy-element multiple bonds. Although this method is common for alkenes, to our knowledge, it is unprecedented for heavier element multiple bonds.[2] As a starting point, we have initiated studies to explore the activation of the P=C bond in phosphaalkenes with cationic initiators.[3] A common cationic polymerization for C=C bonds involves addition of a Lewis acid (e.g. AlCl$_3$) to the double bond, forming a reactive carbocation which acts as the propagating species. In contrast, several modes of coordination have been observed for phosphaalkenes due to the closely spaced π-bond and the phosphorus lone pair energy levels.[3,4] Herein, we report our preliminary investigations of the activation of the P=C bond with possible cationic initiators and our studies of the mechanism of a catalytic intramolecular C−H bond activation reaction.

The ideal precursors to poly(phosphaalkenes) would possess a localized double bond and small substituents at both phosphorus and carbon. Although compounds fulfilling these criteria are known, they often exhibit poor stability under ambient conditions.[5] Thus, a stable and isolable phosphaalkene was sought for detailed studies of possible initiation reactions. Compound **1** (2,4,6-tri-*tert*-butylphenyl = Mes*), which possesses a single sterically demanding substituent, was prepared according to the procedure of Appel and co-workers.[6] Interestingly, this compound was the first phosphaalkene to form an η^1:η^2 complex with two coordinated iron(0) centers.[6]

The possible cationic activation of **1** was probed by treating it with GaCl$_3$ (1 equiv) in CH$_2$Cl$_2$. Analysis of the reaction mixture by ^{31}P NMR spectroscopy, surprisingly, revealed quantitative consumption of **1** (δ 289.0) and the formation of a new species with a doublet resonance at 16.4 ppm ($^1J_{PH}$ = 498 Hz).[7] The large coupling constant was attributed to a direct P−H bond. A signal at 7.4 ppm ($^1J_{PH}$ = 498 Hz; 1 H), assigned to a



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2a (M=Ga)
2b (M=Al)

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[1] For reviews, see: Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939. Norman, N. C. *Polyhedron* **1993**, *12*, 2431. Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90. Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217. Regitz, M. *Chem. Rev.* **1990**, *90*, 191. West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924.

[2] See for example: Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1992. Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.

[3] For reviews, see: Appel, R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, 1990; pp 157−219. Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: New York, 1998. Nixon, J. F. *Chem. Rev.* **1988**, *88*, 1327. Mathey, F. *Acc. Chem. Res.* **1992**, *25*, 90. Weber, L. *Eur. J. Inorg. Chem.* **2000**, 2425. Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.

[4] Most studies of the coordination chemistry of phosphaalkenes have involved transition metals. Selected recent examples: Jouaiti, A.; Geoffroy, M.; Terron, G.; Bernardinelli, G. *J. Am. Chem. Soc.* **1995**, *117*, 2251. Hobbold, M.; Streubel, R.; Benvenutti, M. H. A.; Hitchcock, P. B.; Nixon, J. F. *Organometallics* **1997**, *16*, 3726. Benvenutti, M. H. A.; Cenac, N.; Nixon, J. F. *Chem. Commun.* **1997**, 1327. van der Sluis, M.; Beverwijk, V.; Termaten, A.; Bickelhaupt, F.; Kooijman, H.; Spek, A. L. *Organometallics* **1999**, *18*, 1402. Ikeda, S.; Ohhata, F.; Miyoshi, M.; Tanaka, R.; Minami, T.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4512. Bridgeman, A. J.; Mays, M. J.; Woods, A. D. *Organometallics* **2001**, *20*, 2076. Weber, L.; Dembeck, G.; Lönneke, P.; Stammler, H.; Neumann, B. *Organometallics* **2001**, *20*, 2288.

[5] Gaumont, A. C.; Denis, J. M. *Chem. Rev.* **1994**, *94*, 1413.

[6] Appel, R.; Casser, C.; Immenkeppel, M.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 895.

[7] Synthesis of **2a**: under an inert atmosphere, GaCl$_3$ (0.303 g, 1.72 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise to a stirred solution of **1** (0.500 g, 1.72 mmol) in CH$_2$Cl$_2$ (40 mL) at 20 °C. After the mixture was stirred overnight, the solvent was removed in vacuo, yielding a colorless powder. The product was recrystallized by slow evaporation of a concentrated CH$_3$CN solution. Yield: 0.650 g (81%). ^{31}P NMR (CDCl$_3$, 300 K): δ 16.4 ppm (d, $^1J_{PH}$ = 498 Hz). ^{1}H NMR (CDCl$_3$, 300 K): δ 7.60 (d, 1H, $^4J_{HP}$ = 5.8 Hz, *m-H*), 7.4 (dm, 1H, $^1J_{HP}$ = 498 Hz, P*H*), 7.28 (s, 1H, *m-H*), 2.84 (dd, 2H, $^2J_{HP}$ = 11.4 Hz, $^3J_{HH}$ = 4.6 Hz, PC*H*$_2$C(CH$_3$)$_2$), 1.93 (m, 2H, PC*H*$_2$Ga), 1.51 (s, 6H, C(C*H*$_3$)$_2$), 1.48 (s, 9H, *o*-^{t}Bu), 1.34 (s, 9H, *p*-^{t}Bu). Anal. Calcd for C$_{19}$H$_{31}$Cl$_3$GaP: C, 48.92; H, 6.70; Cl, 22.80. Found: C, 49.09; H, 6.90; Cl, 22.83.

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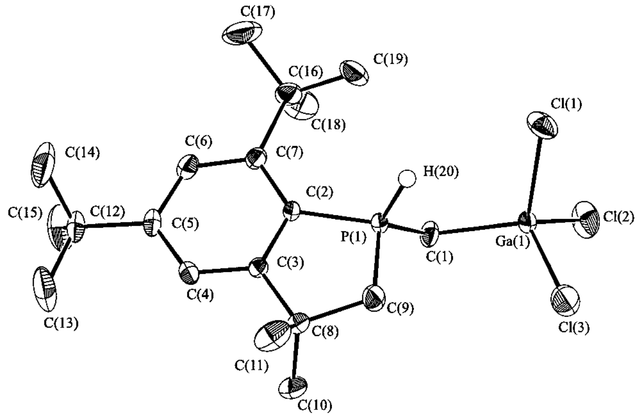
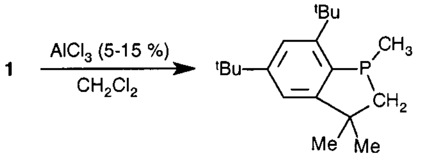


Figure 1. Molecular structure of an enantiomer of **2a** (50% probability). Selected bond lengths (Å) and angles (deg): P(1)−C(1) = 1.773(3), P(1)−C(2) = 1.786(3), P(1)−C(9) = 1.793(4), Ga(1)−C(1) = 1.994(3); P(1)−C(1)−Ga(1) = 112.70(14).

P−H moiety, was observed in the ^{1}H NMR spectrum in $CDCl_3$. In addition, the aliphatic region of the ^{1}H NMR spectrum showed three singlet resonances for methyl groups (δ 1.51, 6H; 1.48, 9H and 1.34, 9H), suggesting C−H activation of one of the *o-tert*-butyl CH_3 groups. Colorless crystals suitable for X-ray crystallography were obtained upon slow evaporation of a solution of the product in acetonitrile. The molecular structure (Figure 1)[8] confirmed the suspected intramolecular C−H activation and the zwitterionic nature of **2a**, which can be envisaged as a coordinated ylide.

The reaction of **1** with substoichiometric quantities of $GaCl_3$ (0.05 equiv) yielded small quantities of **2a** and starting material **1**. However, when a solution of **1** in CH_2Cl_2 was treated with $AlCl_3$ (0.05 equiv) and monitored by ^{31}P NMR spectroscopy, remarkably, the formation of a single product was observed. The reaction proceeded to completion over 5 days, and the phosphine product **3** ($\delta_{^{31}P} = -28.0$) was isolated and its identity confirmed by NMR and MS.[9] Interestingly, when larger quantities of $AlCl_3$ (0.10 and 0.15 equiv) were employed, signals for **2b** (δ 16.9; $^1J_{PH} = 489$ Hz) were initially detected. In each case, after approximately 8 days of monitoring by ^{31}P NMR spectroscopy, **1** and **2b** were consumed and **3** was formed quantitatively. Thus, we infer that **2b** must be an intermediate in the catalytic reaction. We speculate that the presence of an acidic P−H bond adjacent to the organometallic fragment allows for facile formation of **3** and regeneration of $AlCl_3$, which can further activate **1**.



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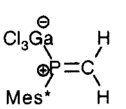
Although intramolecular C−H activation of the Mes* group with electrophiles is reasonably common in low-coordinate phosphorus chemistry,[10,11] to our knowledge, catalytic C−H activation has not been reported for reactions of phosphaalkenes. The mechanism of C−H activation was investigated using low-temperature NMR spectroscopy. Due to the poor solubility of $AlCl_3$ in d_2-methylene chloride at low temperatures, $GaCl_3$ was chosen for these studies. Thus, CD_2Cl_2 was added to a cooled NMR tube (163 K) containing a solid mixture of $GaCl_3$ and **1** (1:1) and the reagents were dissolved upon warming to 193 K. Remarkably, the ^{31}P NMR spectrum showed the quantitative formation of a singlet resonance at 208.9 ppm.[12,13] Two possible modes of coordination (structures **4** and **5**) are considered most likely upon consideration of the electronic structure of phosphaalkenes.[14] However, on the basis of electronegativity differences ($\chi_C > \chi_P$), steric hindrance at phosphorus, and the bond connectivity in the final product (**2a**), compound **5** might initially be presumed the intermedi-



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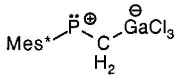

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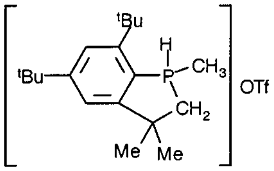

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[8] Crystal data for $C_{19}H_{31}Cl_3GaP$ (**2a**): $P\bar{1}$, $a = 10.0454(6)$ Å, $b = 11.0240(7)$ Å, $c = 11.1410(9)$ Å, $\alpha = 94.935(4)°$, $\beta = 112.222(3)°$, $\gamma = 94.093(2)°$, $V = 1130.6(1)$ Å^3, $Z = 2$, μ(Mo Kα) = 16.41 cm^{-1}, $d_{calcd} = 1.370$ g cm^{-3}, 173(1) K. Details of the data collection and refinement: Rigaku/ADSC CCD diffractometer with graphite monochromator, colorless needle (0.25 × 0.10 × 0.05 mm) mounted on a glass fiber. Of 10 364 reflections collected ($2\theta = 5.1-55.8°$), 4599 were unique ($R_{int} = 0.043$). Solution was by direct methods, and non-hydrogen atoms were refined anisotropically; hydrogen atoms were included but not refined. R1 = 0.037, wR2 = 0.092, GOF = 1.07, $\Delta\rho_{max} = 0.47$ e Å^{-3}.

[9] Characterization data for **3** are as follows. ^{31}P NMR ($CDCl_3$, 300 K): δ −28.0 (s). ^{1}H NMR ($CDCl_3$, 300 K): δ 7.49 (m, 1H, *m-H*), 7.25 (s, 1H, *m-H*), 2.26 (m, 2H, $PCH_2C(CH_3)_2$), 1.97 (d, 3H, $^2J_{HP} = 14.6$ Hz, PCH_3), 1.66 (s, 9H, *o*-^{t}Bu), 1.57, 1.53 (s, 6H, $C(CH_3)_2$), 1.50 (s, 9H, *p*-^{t}Bu). MS (EI, 70 eV): *m/z* [%] 291, 290 [19, 81; M$^+$]; 276, 275 [16, 81; M$^+$ − CH_3]; 249, 248 [24, 100; M$^+$ − $C(CH_3)_2$]; 234, 233 [13, 43; M$^+$ − $C(CH_3)_3$]; 58, 57 [3, 31; $C(CH_3)_3$].

[10] See for example: (a) Cowley, A. H.; Pakulski, M. K. *J. Am. Chem. Soc.* **1984**, *106*, 1491. (b) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1801. (c) Karsch, H. H.; Reisacher, H. U.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 454. (d) Yoshifuji, M.; Sato, T.; Inamoto, N. *Chem. Lett.* **1988**, 1735. (e) Gouygou, M.; Tachon, C.; Etemad-Moghadam, G.; Koenig, M. *Tetrahedron Lett.* **1989**, *30*, 7411. (f) Cowley, A. H.; Gabbaï, F.; Schluter, R.; Atwood, D. *J. Am. Chem. Soc.* **1992**, *114*, 3142. (g) Shah, S.; Simpson, M. C.; Smith, R. C.; Protasiewicz. J. D. *J. Am. Chem. Soc.* **2001**, *123*, 6925. (h) Stradiotto, M.; Fujdala, K. L.; Tilley, T. D. *Helv. Chim. Acta* **2001**, *84*, 2958.

[11] Reaction of the nucleophile BuLi with the phosphaalkene Mes*P=CBr_2 resulted in low yields of an interesting intramolecular C−H activation product: Ito, S.; Toyota, K.; Yoshifuji, M. *Chem. Commun.* **1997**, 1637.

[12] Characterization data for **4** are as follows. ^{31}P NMR (CD_2Cl_2, 193 K): δ 208.9. ^{1}H NMR (CD_2Cl_2, 193 K): δ 7.5 (s, 2H, *m-H*), 7.5 (d, 1H, $^2J_{HH} = 8$ Hz, P=C*H*), 7.1 (d, 1H, $^2J_{HH} = 8$ Hz, P=C*H*), 1.5 (s, 18H, *o*-^{t}Bu), 1.3 (s, 9H, *p*-^{t}Bu). ^{13}C NMR (CD_2Cl_2, 193 K): δ 156.4 (s, *o*-Ar), 155.0 (s, *p*-Ar), 148.7 ppm (d, $^1J_{CP} = 51$ Hz, P=CH_2), 123.3 (d, $^3J_{CP} = 8.1$ Hz, *m*-Ar), 117.5 (d, $^1J_{CP} = 13.6$ Hz, *i*-Ar), 37.5 (s, *o*-*C*Me$_3$), 34.9 (s, *p*-*C*Me$_3$), 33.0 (s, *o*-C(CH_3)$_3$), 30.1 (s, *p*-C(CH_3)$_3$).

[13] This intermediate was stable in solution for several days if stored at 193 K; however, **2a** is detected after a few minutes at 233 K.

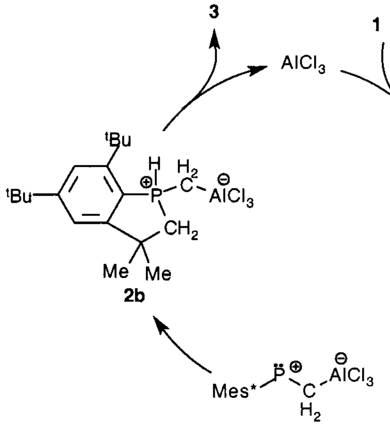
[14] The electronic structure of phosphaalkenes has been studied extensively using photoelectron spectroscopy and molecular modeling. The two filled frontier orbitals (the lone pair on phosphorus and the (2p−3p)π bond) are closely spaced in energy, and the order is highly dependent on the nature of the substituents. (See, for example: Lacombe, S.; Gonbeau, D.; Cabioch, J.-L.; Pellerin, B.; Denis, J.-M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964 and references therein).

ate. We are aware of one previous study of the reaction of phosphaalkenes with group 13 Lewis acids where an adduct through the phosphorus lone pair of $^{t}BuP{=}C(^{t}Bu)$ was observed with $AlCl_3$ ($\delta_{^{31}P}$ 200.5).[15] Interestingly, the chemical shift we observe (208.9 ppm) is remarkably close to that of $^{t}Bu(Cl_3Al)P{=}C(^{t}Bu)H$. Moreover, the ^{1}H NMR spectrum of the intermediate showed inequivalent methylene hydrogens (7.5 and 7.1 ppm; $^{2}J_{HH} = 8$ Hz), and a signal was observed at 148.7 ppm (d, $^{1}J_{CP} = 51$ Hz) in the ^{13}C NMR spectrum, both consistent with a $P{=}CH_2$ moiety. Therefore, we postulate that the observed intermediate is **4**; however, it is likely that phosphenium species **5** is present either in equilibrium with **4** or as a fleeting species in the formation of **2a**.

Further evidence for a phosphenium species as a key intermediate in the C−H activation was obtained from an isotopic labeling study for the analogous reaction of **1** with triflic acid to obtain **6**.[16] When **1** was treated with DOTf (1 equiv) in CD_2Cl_2, both ^{31}P and ^{1}H NMR spectra showed quantitative formation of **6** with a $-CH_2D$ group and a P−H bond. Therefore, even if a P−D species is formed initially (cf. **4**), oxidative addition of C−H *must* occur from a phosphenium cation after 1,2-deuterium migration from P to C.[17] In the reaction of **1** with $GaCl_3$, although **4** is detected at low temperatures, we believe that $GaCl_3$ migrates from P to C, forming phosphenium **5** prior to C−H oxidative addition, which yields zwitterionic **2a**. Based on these observations, we propose the cycle given in Scheme 1 for the conversion of **1** to **3** facilitated by catalytic amounts of $AlCl_3$. The rate-determining step is likely the dissociation of $AlCl_3$ from complex **2b**, which explains why larger amounts of $AlCl_3$ result in slower reactions.

The involvement of a phosphenium species in these reactions is interesting since unstable divalent phosphorus cations were postulated for the reactions of diphosphenes [Mes*P=PMes*] with electrophiles;[10b] recently the first stable phosphanyl phosphenium ion, [Mes*P=P(Me)Mes*]OTf, was isolated in the reaction of the diphosphene with MeOTf.[18] Furthermore, the preparation of divalent phosphorus cations, like their carbene congeners, has attracted considerable attention; however, stable carbenes and phosphenium ions must possess at least one π-donor substituent (i.e. NR'_2).[19,20] There is one previous report of a non-resonance-stabilized phosphenium ion from the reaction of a phosphaalkene with an electrophile,[21] generating the known species $[(Me_5C_5)P(C(SiMe_3)_2H)]^+$, which subsequently undergoes an intramolecular C−H activation reaction.[22] We are interested in phosphenium **5**, since it would represent the desired propagating species for a cationic polymerization for phosphaalkenes. Thus, our future studies will investigate the use of other substituents which may prevent intramolecular reactions and possibly favor intermolecular reactions.

Scheme 1. Proposed Reaction Pathway for the Intramolecular C−H Bond Activation of 1 with Catalytic $AlCl_3$ To Form 3



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Supporting Information Available: Text giving details of the X-ray structure determination and tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Niecke, E.; Symalla, E. *Chimia* **1985**, *39*, 320.

[16] Synthesis of **6**: the same procedure as for **2a** was followed; HO_3SCF_3 (0.284 g; 1.89 mmol), **1** (0.500 g; 1.72 mmol). The product was recrystallized from CH_3CN/toluene (3:1) at −40 °C. Yield: 0.450 g (59%). ^{31}P NMR ($CDCl_3$, 300 K): δ 13.6 ppm (d, $^{1}J_{PH} = 539$ Hz). ^{1}H NMR ($CDCl_3$, 300 K): δ 7.84 (dqdd, 1H, $^{1}J_{HP} = 538$ Hz, $^{3}J_{HH} = 5.4$ Hz (to CH_3), $^{3}J_{HH} = 5.0$ and 1.9 Hz (to CH_2), P−*H*), 7.55 (d, 1H, $^{4}J_{HP} = 5.8$ Hz, *m-H*), 7.20 (s, 1H, *m-H*), 2.95 (dm, 1H, $^{2}J_{HP} = 15.8$ Hz, 1H in PCH_2), 2.68 (dm, 1H, $^{2}J_{HP} = 13.5$ Hz, 1H in PCH_2), 2.30 (dd, 3H, $^{2}J_{HP} = 15.0$ Hz, $^{3}J_{HH} = 5.1$ Hz, CH_3), 1.49 (s, 6H, $C(CH_3)_2$), 1.42 (s, 9H, *o*-^{t}Bu), 1.29 (s, 9H, *p*-^{t}Bu). ^{19}F NMR ($CDCl_3$, 300 K): −78.9 ppm (s, CF_3).

[17] If C−H oxidative addition occurred prior to 1,2-deuterium migration, a mixture of **6** with P−D and P−H would be obtained.

[18] Loss, S.; Widauer, C.; Grützmacher, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3329.

[19] (a) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. (b) Sanchez, M.; Mazières, M.-R. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Sherer, O. J., Eds.; Thieme: New York, 1990; pp 129−148. (c) Burford, N.; Losier, P.; Macdonald, C.; Kyrimis, V.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 1434. (d) Reed, R. W.; Xie, Z.; Reed, C. A. *Organometallics* **1995**, *14*, 5002. (e) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828.

[20] The first examples of stable carbenes bearing a "spectator" substituent have recently been reported. This paper also reports intramolecular C−H activation of one of the *o*-*tert*-butyl groups of a Mes* substituent by the carbene center, similar to that observed in the present study. See: Solé, S.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2001**, *292*, 1901.

[21] Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Chimia* **1985**, *39*, 277.

[22] Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1983**, *105*, 2074.