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Synthesis, Structure, and Reactions of 1-*tert*-Butyl-2-diphenylphosphino-imidazole

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Metalation reactions were studied of a sterically demanding imidazole derivative, namely, 1-*tert*-butylimidazole (**1**), with different metalation reagents and subsequent reaction with diphenylchlorophosphane. The reaction product, 1-*tert*-butyl-2-diphenylphosphino-imidazole (**2**), was subjected to oxidation and complexation reactions to yield the corresponding products Ph_2(Imi)P-E (E = O (**3**), S (**4**), Se (**5**), $W(CO)_5$ (**8**)) and in the case of borane-THF the *N*-BH_3 coordination product **10** was obtained. The analytical data of the new compounds are discussed, including X-ray diffraction studies of **3**−**5**.

Introduction

Phosphorus-containing imidazole derivatives have attracted increasing interest over the years.[1] For example, N^1 substituted derivatives,[2] which are of particular interest as many natural products and analogues of natural products, for example, nucleotides,[3] are among them and can be easily obtained by reacting an *N*-H imidazole derivative with a diorganochlorophosphane in the presence of triethylamine as base.[4] The C^2 position can also be selectively addressed via metalation reactions as N^1 substituted imidazole derivatives were known to react with, for example, organolithium compounds to give 1,2-disubstituted compounds.[5] The C^2 substituted products have found application as ligands in catalysis, like ethylene oligomerization,[6] alkene isomerizations,[7−10] aryl aminations,[11] Suzuki and Buchwald-Hartwig type reactions,[12] C−H bond activation reactions,[13] hydration of alkynes,[8,10,14−17] or as enzyme model.[18] They have also been used to synthesize different types of mono- and bimetallic complexes.[19,20] Most of the C^4 substituted compounds have been synthesized via cyclization reactions, and only one was obtained by reaction of a Grignard compound with an imidazole derivative.[21−24] Although the differences between deprotonation and halogen-metal exchange reactions have long been studied,[25−29] the influence of the size of the N^1

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(1) A literature search yielded more than 500 N^1 substituted, more than 100 N^1-organyl, C^2 substituted, less than 20 N^1-organyl, C^4 substituted but not a single N^1-organyl, C^5 substituted imidazole derivative with a phosphanyl- or phosphoryl-substituent.

(2) According to the Hantzsch and Widman nomenclature system, the imidazole ring is numbered starting from the nitrogen atom bearing the substitutent with the higher priority in such a way that the two nitrogen atoms receive the smallest possible numbers; 1 and 3.

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substituent had not been the subject of intensive studies. Most of the known C^2 or C^4 substituted imidazole derivatives contain small or sterically non-demanding N^1 substituents such as acetyl,[30] benzyl,[19,23,31] bis(ethoxy)methyl,[30] methyl,[6,32,33] ethyl,[32] *n*-octyl,[22] or phenyl[21,34] Just a few examples with trityl,[11] mesityl,[12] or differently substituted aromatic groups[22,35] were reported. Most often, diphenylchlorophosphane was used[12,31,32,34,35] as it is commercially available and often yields relatively stable derivatives, but also derivatives with other phosphanyl groups having substituents such as *tert*-butyl,[12,33] cyclohexyl,[11,12] isopropyl,[11] chloro,[19] and di(alkylamino)[22,32] were reported.

Here, we present metalation of 1-*tert*-butylimidazole (**1**) and subsequent reaction with diphenylchlorophosphane as well as further studies on the reactivity of the 1-*tert*-butyl-2-diphenylphosphino-imidazole (**2**).

Experimental Section

General Considerations. All reactions except the synthesis of 1-*tert*-butylimidazole (**1**) and the oxidation reactions were carried out under an argon atmosphere, using common Schlenk techniques and dry solvents. Diethyl ether, petrol ether, and tetrahydrofuran (THF) were dried over sodium wire, dichloromethane over calcium hydride, and further purified by subsequent distillation. Diphenylchlorophosphane was distilled prior to use and stored under argon. The $[W(CO)_5(thf)]$ complex was synthesized by irradiating $W(CO)_6$ in THF with a 150 W low-pressure mercury lamp (TQ150, Heraeus Noblelight, Hanau, Germany).[36] All other chemicals were used as received. All NMR spectra were recorded on a Bruker AX-300 spectrometer, with a frequency of 300.1 MHz for ^{1}H. The ^{1}H and ^{13}C spectra were referenced to the residual protons and the ^{13}C signals of the deuterated solvents, the ^{11}B to BF_3*OEt_2 and ^{31}P to 85% H_3PO_4 as external standard, respectively. Melting points were determined in one-sided melted off capillaries using a Büchi Type S apparatus; they are uncorrected. Elemental analyses were carried out on a Vario Type EL gas chromatograph. Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. The Infrared spectra were recorded on a Nicolet 380 FT-IR spectrometer using KBr plates. The UV/vis spectra were recorded in solution on a Shimadzu UV-1650 PC spectrometer. The X-ray analyses were performed on a Nonius Kappa CCD type diffractometer.

Preparation of 1-*tert*-Butylimidazole (1)[37]. In a 100 mL three-necked flask connected to two dropping funnels and a condenser was placed 50 mL of distilled water. One dropping funnel contained a mixture of 40% aqueous glyoxal (11.5 mL, 0.1 mol) and 40% aqueous formaldehyde (8.1 mL, 0.1 mol), the other *tert*-butylamine (10.6 mL, 0.1 mol) and 25% aqueous ammonia (6.8 mL, 0.1 mol). The water was heated until boiling, and then both solutions were added simultaneously. The reaction mixture turned brown and was stirred for 30 min at 100 °C after complete addition and then cooled to room temperature. After removal of the water by rotatory evaporator, the crude product was purified via *vacuum* distillation (bp. 53 °C/0.9 mbar) and obtained as a very pale yellow liquid, yield 70%. Analysis:[38] ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ = 7.00 (s br, 1H, C^2-H), 6.45 (s br, 1H, C^5-H), 6.41 (s br, 1H, C^4-H), 0.90 (s, 9H, C_4H_9); $^{13}C\{^1H\}$-NMR (75.0 MHz, $CDCl_3$, RT): δ = 134.0 (s, C^2), 128.7 (s, C^5), 116.2 (s, C^4), 54.4 (s, *tert*-butyl-C), 30.3 (s, *tert*-butyl-CH_3); MS (EI, 70 eV): *m*/*z* 124 (M^+, 92%), 68 ($M^+ - C_4H_9$, 76%), 57 ($C_4H_9^+$, 42%).

Preparation of 1-*tert*-Butyl-2-diphenylphosphino-imidazole (2). A 100 mL portion of THF and 1-*tert*-butylimidazole (**1**) (1.35 mL, 10 mmol) were placed in a 250 mL Schlenk flask equipped with a septum stopper. The flask was cooled to −80 °C, and *tert*-butyllithium (7 mL, 1.5 M solution in pentane, 10.5 mmol) was slowly added (reaction mixture turned yellow). After 30 min stirring at −80 °C, diphenylchlorophosphane (1.85 mL, 10.3 mmol) was added (and the reaction mixture darkened a little bit). The reaction mixture was slowly warmed up until ambient temperature, the solvent was then removed in vacuo, and the light yellow residue was taken up in dichloromethane. It was filtered through a G3 frit equipped with a layer of Celite to remove the precipitated lithium chloride. The filtrate was concentrated in vacuo (8×10^{-3} mbar), and the crude product was purified by recrystallization from 20 mL of hot toluene. Colorless crystals were obtained, yield 2.00 g (65%), mp 124 °C. Analysis: ^{1}H NMR (300.1 MHz, THF-d_8, 25 °C): δ = 7.58−7.26 (m, 11H, C^5-H and C_6H_5), 7.09 (d, $^3J_{H,H}$ = 1.1 Hz, 1H, C^4-H), 1.80 (s, 9H, C_4H_9); $^{13}C\{^1H\}$ NMR (75.0 MHz, THF-d_8, 25 °C): δ = 144.5 (d, $^1J_{P,C}$ = 8.7 Hz, C^2), 138.0 (d, $^1J_{P,C}$ = 5.5 Hz, *ipso*-phenyl), 134.3 (d, $^2J_{P,C}$ = 21.0 Hz, *ortho*-phenyl), 129.3 (d, $^{3+4}J_{P,C}$ = 2.3 Hz, C^5), 128.6 (s, *para*-phenyl), 128.1 (d, $^3J_{P,C}$ = 7.3 Hz, *meta*-phenyl), 120.0 (d, $^{3+4}J_{P,C}$ = 1.9 Hz, C^4), 57.0 (d, $^3J_{P,C}$ = 1.3 Hz, *tert*-butyl-C), 31.4 (d, $^4J_{P,C}$ = 12.0 Hz, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, THF-d_8, 25 °C): −23.6 (quin, $^3J_{P,H}$ = 7.6 Hz); MS (EI, 70 eV): *m*/*z* 308 (M^+, 64%), 251 ($M^+ - C_4H_9$, 100%), 183 ($P(C_6H_5)_2^+$, 40%); IR (KBr): $\tilde{\nu}$ = 2983 (m, ν(CH), 1477 (m, ν(CN)), 1434 (s, ν(P−C_6H_5)), 1246 (vs, δ(CH-C_4H_9)), 754 + 748 (vs, δ(CH-C_6H_5)), 697.3 (vs, δ(ring-C_6H_5)); UV/vis (CH_2Cl_2): λ_{max} = 205 nm; EA: calcd C 74.01, H 6.86, N 9.08, found C 73.73, H 6.88, N 8.89; R_f-value (1:1 diethyl ether/petrol ether): 0.683.

Preparation of 1-*tert*-Butyl-2-diphenylphosphoryl-imidazole (3). Twenty milliliters of CH_2Cl_2 and 1-*tert*-butyl-2-diphenylphosphino-imidazole (**2**) (617 mg, 2 mmol) were placed in a 50 mL round-bottom flask. To it, meta-chloroperoxybenzoic acid (345 mg, 2 mmol) was added, and the reaction mixture was stirred for 30 min at ambient temperature. The solvent was removed in vacuo (8×10^{-3} mbar), and the colorless residue was purified via column chromatography at ambient temperature, using aluminum oxide (90 active neutrale) as stationary phase and petrol ether/diethyl ether-mixture as eluents. A colorless solid was obtained, yield 467 mg (72%), mp 145 °C. Analysis: ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ = 7.77−7.43 (m, 10H, C_6H_5-H), 7.28 (pt, $^{3+4}J_{H,H}$ = 1.2 Hz, 1H, C^5-H), 7.19 (pt, $^{3+4}J_{H,H}$ = 1.2 Hz, 1H, C^4-H), 1.76 (s, 9H, C_4H_9); $^{13}C\{^1H\}$-NMR (75.0 MHz, $CDCl_3$, 25 °C): δ = 139.4 (d, $^1J_{P,C}$ = 147.7 Hz, C^2), 133.0 (d, $^1J_{P,C}$ = 113.2 Hz, *ipso*-phenyl), 130.9 (d, $^2J_{P,C}$ = 9.7 Hz, *ortho*-phenyl), 130.6 (d, $^4J_{P,C}$ = 2.9 Hz, *para*-phenyl), 127.5 (d, $^{3+4}J_{P,C}$ = 18.1 Hz, C^5), 127.3 (d, $^3J_{P,C}$ = 12.6 Hz, *meta*-phenyl), 120.8 (d, $^{3+4}J_{P,C}$ = 3.2 Hz, C^4), 57.5 (s, *tert*-butyl-C), 30.3 (s, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, $CDCl_3$, 25 °C): 21.7 (quin, $^3J_{P,H}$ = 12.1 Hz); MS (EI, 70 eV): *m*/*z* 324 (M^+, 64%), 268 ($M^+ - C_4H_9$, 100%), 191 ($M^+ - C_4H_9 - C_6H_5$, 65%);): exact mass calcd 324.1389 found 324.1391; IR (KBr): $\tilde{\nu}$ = 3049 (w, ν(CH)), 2983 (m, ν(CH)), 1476 (m, ν(CN)), 1440 (vs, ν(P−C_6H_5)), 1254 (vs, ν(PO)); UV/vis (CH_2Cl_2): λ_{max} = 209 nm; EA: calcd C 70.36, H 6.53, N 8.64, found C 69.01, H 6.37, N 8.65.

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Preparation of 1-*tert*-Butyl-2-diphenylthiophosphoryl-imidazole (4) and 1-*tert*-Butyl-2-diphenylselenophosphoryl-imidazole (5). Ten milliliters of toluene, 1-*tert*-butyl-2-diphenylphosphino-imidazole (**2**) (927 mg, 3 mmol), and elemental sulfur or selenium (96/237 mg, 3 mmol) were placed in a 50 mL round-bottom flask equipped with a condenser. The reaction mixture was heated for 3 h at 110 °C and then slowly cooled to ambient temperature. The product was precipitated from the reaction mixture in the form of colorless crystals. The crystals were washed with *n*-pentane and dried in vacuo (8×10^{-3} mbar). Yield: (**4**) 951 mg (93%), (**5**) 1057 mg (91%), mp (**4**) 174 °C, (**5**) 204 °C. Analysis: (**4**) ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ = 7.66−7.34 (m, 10H, C_6H_5-H), 7.27 (pt, $^{3+4}J_{H,H}$ = 1.4 Hz, 1H, C^5-H), 7.05 (pt, $^{3+4}J_{H,H}$ = 1.4 Hz, 1H, C^4-H), 1.72 (s, 9H, C_4H_9); ^{13}C{^{1}H}-NMR (75.0 MHz, $CDCl_3$, 25 °C): δ = 138.9 (d, $^1J_{P,C}$ = 129.0 Hz, C^2), 133.3 (d, $^1J_{P,C}$ = 94.0 Hz, *ipso*-phenyl), 131.1 (d, $^2J_{P,C}$ = 10.6 Hz, *ortho*-phenyl), 130.3 (d, $^4J_{P,C}$ = 3.0 Hz, *para*-phenyl), 127.5 (d, $^{3+4}J_{P,C}$ = 18.0 Hz, C^5), 127.2 (d, $^3J_{P,C}$ = 13.0 Hz, *meta*-phenyl), 122.4 (d, $^{3+4}J_{P,C}$ = 2.5 Hz, C^4), 58.3 (s, *tert*-butyl-C), 30.6 (s, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, $CDCl_3$, 25 °C): 39.5 (quin, $^3J_{P,H}$ = 13.3 Hz); MS (EI, 70 eV): *m*/*z* 340 (M^+, 50%), 307 (M^+-S, 5%), 284 ($M^+ - C_4H_9$, 100%);): exact mass calcd 340.1160 found 340.1163; IR (KBr): $\tilde{\nu}$ = 3103 (w, ν(CH)), 2971 (m, ν(CH)), 1436 (vs, ν(P−C_6H_5)), 650 (vs, ν-(PS)); UV/vis (CH_2Cl_2): λ_{max} = 209 nm; EA: calcd C 67.04, H 6.22, N 8.23, found C 65.54, H 6.21, N 8.06.

(**5**) ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ = 7.77−7.15 (m, 12H, C^4/C^5-H and C_6H_5), 1.72 (s, 9H, C_4H_9); ^{13}C{^{1}H}-NMR (75.0 MHz, $CDCl_3$, 25 °C): δ = 137.2 (d, $^1J_{P,C}$ = 119.0 Hz, C^2), 132.2 (d, $^1J_{P,C}$ = 84.7 Hz, *ipso*-phenyl), 131.7 (d, $^2J_{P,C}$ = 11.0 Hz, *ortho*-phenyl), 130.4 (d, $^4J_{P,C}$ = 3.2 Hz, *para*-phenyl), 127.7 (d, $^{3+4}J_{P,C}$ = 17.5 Hz, C^5), 127.2 (d, $^3J_{P,C}$ = 13.3 Hz, *meta*-phenyl), 122.8 (d, $^{3+4}J_{P,C}$ = 2.3 Hz, C^4), 58.5 (s, *tert*-butyl-C), 30.8 (s, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, $CDCl_3$, 25 °C): 30.6 $^1J_{Se,P}$ = 740.0 Hz (quin, $^3J_{P,H}$ = 7.6 Hz); MS (EI, 70 eV): *m*/*z* 388 (M^+, 57%), 332 ($M^+ - C_4H_9$, 52%), 308 (M^+ − Se, 44%);): exact mass calcd 384.0631 found 388.0608; IR (KBr): $\tilde{\nu}$ = 3102 (w, ν(CH)), 2970 (w, ν(CH)), 1477 (m, ν(CN)), 1436 (vs, ν(P−C_6H_5)), 754 + 686 (vs, δ(C_6H_5)); UV/vis (CH_2Cl_2): λ_{max} = 210 nm; EA: calcd C 58.92, H 5.46, N 7.23, found C 58.82, H 5.41, N 7.03.

Preparation of 1-*tert*-Butyl-2-diphenylphosphino-3-methyl-imidazolium Iodide (7). A 100 mL portion of THF and 1-*tert*-butyl-3-methyl-imidazolium iodide (**6**) (3.87 g, 14.8 mmol), prepared from the reaction of 1-*tert*-butylimidazole (**1**) with iodomethane in boiling methanol,[39] were placed in a 250 mL Schlenk flask equipped with a septum stopper. The flask was cooled to −80 °C, and *tert*-butyllithium (22.2 mL, 1.5 M solution in pentane, 14.8 mmol) was slowly added (reaction mixture turned deep yellow). After 45 min stirring at −80 °C, diphenylchlorophosphane (2.66 mL, 14.8 mmol) was added (reaction mixture turned blood-red). The reaction mixture was slowly warmed up until room temperature. The solvent was removed in vacuo (8×10^{-3} mbar), and the obtained dark-red slurry was taken up in 20 mL of distilled water to remove the formed lithium chloride; the red color disappeared. The solid was washed multiple times with water and then *n*-pentane. The hygroscopic solid was dried in vacuo (8×10^{-3} mbar), yield 5.91 g (89%), mp 190 °C. Analysis: ^{1}H NMR (300.1 MHz, DMSO-d_6, 25 °C): δ = 7.57−7.30 (m, 12H, C^4/C^5-H and C_6H_5), 3.75 (s, 3H, N−CH_3), 1.62 (s, 9H, C_4H_9); ^{13}C{^{1}H}-NMR (75.0 MHz, DMSO-d_6, 25 °C): δ = 139.0 (s br, C^2), 131.9 (d, $^1J_{P,C}$ = 5.2 Hz, *ipso*-phenyl), 133.1 (d, $^2J_{P,C}$ = 20.5 Hz, *ortho*-phenyl), 130.1 (s, *para*-phenyl), 129.3 (d, $^3J_{P,C}$ = 7.5 Hz, *meta*-phenyl), 128.4 (d, $^{3+4}J_{P,C}$ = 6.5 Hz, C^5), 125.8 (d, $^{3+4}J_{P,C}$ = 4.5 Hz, C^4), 60.0 (s, *tert*-butyl-C), 34.9 (d, $^3J_{P,C}$ = 10.0 Hz, N−CH_3), 28.9 (s br, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, DMSO-d_6, 25 °C): −35.0 (quin br, $^3J_{P,H}$ = 7.7 Hz); MS (ESI): exact mass calcd 323.1672 found 323.1674 (as $C_{20}H_{24}N_2P^+$); IR (KBr): $\tilde{\nu}$ = 2978 (w, ν(CH)), 1434 (s, ν(P−C_6H_5)), 746 + 700 (vs, δ(C_6H_5)); UV/vis (CH_2Cl_2): λ_{max} = 231 nm.

Reaction of 1-*tert*-Butyl-2-diphenylphosphino-imidazole (2) with [W(CO)$_5$(thf)] Complex. To a freshly prepared THF solution of [W(CO)$_5$(thf)][36] complex (1 mmol), prepared by irradiating $W(CO)_6$ in THF with a 150 W low-pressure mercury lamp for 30 min at 10 °C, was added a solution of 1-*tert*-butyl-2-diphenylphosphino-imidazole (**2**) (309 mg, 1 mmol) in 10 mL of THF at ambient temperature in a Schlenk flask. The reaction mixture was stirred at ambient temperature, and the reaction was monitored with ^{31}P NMR. Observed products: **8**: 21.3 ($^1J_{W,P}$ = 254.3 Hz) and **9**: 14.4 ($^1J_{W,P}$ = 193.3 Hz). Analysis: (**8**) ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): δ = 7.49−7.42 (m, 4H, *ortho*-C_6H_5), 7.18 (d, $^3J_{H,H}$ = 1.3 Hz, 1H, C^5-H), 6.94−6.88 (m, 6H, *meta*/*para*-C_6H_5), 6.78 (d, $^3J_{H,H}$ = 1.3 Hz, 1H, C^4-H), 0.67 (s, 9H, C_4H_9); ^{13}C{^{1}H}-NMR (75.0 MHz, C_6D_6, 25 °C): δ = 200.0 (d, $^1J_{W,C}$ = 24.6 Hz, *trans*-CO), 197.3 (d, $^1J_{W,C}$ = 7.1 Hz, *cis*-CO), 139.3 (d, $^1J_{P,C}$ = 66.6 Hz, C^2), 135.6 (d, $^1J_{P,C}$ = 40.1 Hz, *ipso*-phenyl), 130.7 (d, $^2J_{P,C}$ = 11.6 Hz, *ortho*-phenyl), 129.9 (d, $^{3+4}J_{P,C}$ = 1.9 Hz, C^5), 128.7 (d, $^4J_{P,C}$ = 1.9 Hz, *para*-phenyl), 129.3 (d, $^3J_{P,C}$ = 9.7 Hz, *meta*-phenyl), 123.9 (s br, C^4), 57.1 (d, $^3J_{P,C}$ = 1.3 Hz, *tert*-butyl-C), 30.2 (s, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, C_6D_6, 25 °C): 21.3 ($^1J_{W,P}$ = 254.3 Hz); MS (EI, 70 eV): *m*/*z* 604 (M^+ − CO, 20%), 548 (M^+ − 3CO, 76%), 520 (M^+ − 4CO, 50%), 492 (M^+ − 5CO, 92%), 308 (M^+ − $W(CO)_5$, 50%), 251 ($M^+ - W(CO)_5 - C_4H_9$, 100%), 183 (W, 40%), R_f-value (1: 1 diethyl ether/petrol ether): 0.242.

(**9**) mp 95 °C, ^{1}H NMR (300.1 MHz, CD_3CN, −30 °C): δ = 7.69−7.55 (m, 10H, C_6H_5), 7.45 (pt, $^3J_{H,H}$ = 1.2 Hz, 1H, C^5-H), 7.30 (pt, $^3J_{H,H}$ = 1.2 Hz, 1H, C^4-H), 1.19 (s, 9H, C_4H_9); ^{13}C{^{1}H}-NMR (75.0 MHz, CD_3CN, −30 °C): δ = 216.2 (s_{sat}, $^1J_{W,C}$ = 184.5 Hz, CO_{ax}), 208.5 (s_{sat}, $^1J_{W,C}$ = 167.5 Hz, CO_{eq}), 200.9 (s_{sat}, $^1J_{W,C}$ = 132.6 Hz, CO_{eq}), 148.5 (d, $^1J_{P,C}$ = 28.9 Hz, C^2), 133.2 (d, $^1J_{P,C}$ = 20.9 Hz, *ipso*-phenyl), 132.5 (d, $^1J_{P,C}$ = 13.9 Hz, *ortho*-phenyl), 132.1 (d, $^4J_{P,C}$ = 2.0 Hz, *para*-phenyl), 129.8 (d, $^3J_{P,C}$ = 9.9 Hz, *meta*-phenyl), 125.8 (s, C^5), 121.3 (s br, C^4), 61.9 (s, *tert*-butyl-C), 30.1 (s, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, CD_3CN, −30 °C): 10.6 ($^1J_{W,P}$ = 187.6 Hz); MS (EI, 70 eV): *m*/*z* 604 (M^+, 9%), 548 (M^+ − 2CO, 37%), 520 (M^+ − 3CO, 40%), 492 (M^+ − 4CO, 76%), 308 ($M^+ - W(CO)_4$, 46%), 251 ($M^+ - W(CO)_5 - C_4H_9$, 100%), 183 (W, 48%); IR (KBr): $\tilde{\nu}$ = 2007 (s, ν(CO)), 1917(s, ν(CO)), 1875 (s, ν(CO)), 1811 (s, ν(CO)), 1438 (s, ν(P−C_6H_5)); UV/vis (CH_2Cl_2): λ_{max} = 232 nm.

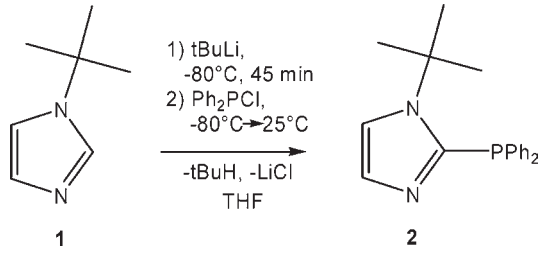
Preparation of 1-*tert*-Butyl-2-diphenylphosphino-3-borane-imidazole (10). Twenty milliliters of THF and 1-*tert*-butyl-2-diphenylphosphino-imidazole (**2**) (617 mg, 2 mmol) were placed in a 50 mL Schlenk flask. Borane THF complex (2 mL, 2 mmol, 1 M solution in THF) was added, and the reaction mixture was stirred for 3 h at ambient temperature. The solvent was removed in vacuo (8×10^{-3} mbar), and the colorless residue was washed multiple times with *n*-pentane. After drying in vacuo (8×10^{-3} mbar), a colorless solid was obtained, yield 580 mg (90%), mp 130 °C. Analysis: ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ = 7.57−7.21 (m, 12H, C^4/C^5-H and C_6H_5), 1.89 (s br, 9H, C_4H_9), 1.66 (s br, 3H, BH_3); ^{11}B{^{1}H}-NMR (96.3 MHz, $CDCl_3$, 25 °C): δ = −20.6; ^{13}C{^{1}H}-NMR (75.0 MHz, $CDCl_3$, 25 °C): δ = 141.3 (d, $^1J_{P,C}$ = 40.1 Hz, C^2), 133.4 (d, $^1J_{P,C}$ = 21.3 Hz, *ipso*-phenyl), 132.4 (d, $^2J_{P,C}$ = 20.7 Hz, *ortho*-phenyl), 131.7 (d, $^{3+4}J_{P,C}$ = 5.2 Hz, C^5), 130.0 (s, *para*-phenyl), 127.7 (d, $^3J_{P,C}$ = 29.1 Hz, *meta*-phenyl), 120.0 (d, $^{3+4}J_{P,C}$ = 3.2 Hz, C^4), 59.5 (s, *tert*-butyl-C), 30.6 (d, $^4J_{P,C}$ = 13.6 Hz, *tert*-butyl-CH_3); ^{31}P NMR (121.5 Hz, $CDCl_3$, 25 °C): −19.5 (s br); MS (ESI): exact mass calcd 345.1664 found 345.1669 (as $C_{19}H_{24}BN_2PNa^+$); IR (KBr): $\tilde{\nu}$ = 3048 (w, ν(CH)), 2981 (m, ν(CH)), 2413 (ν(BH) E), 2363 (ν(BH) A′), 1435 (vs, ν(P−C_6H_5)), 756 + 692 (s, δ(C_6H_5)); UV/vis (CH_2Cl_2): λ_{max} = 210 nm.

(39) Yoshida, Y.; Baba, O.; Larriba, C.; Saito, G. *J. Phys. Chem. B* **2007**, *111*, 12204–12210.

Table 1. Selected NMR Data (Chemical Shifts and Coupling Constants) and Melting Points of Compounds **2**, **3**−**5**

data	**2**	**3**	**4**	**5**
^{31}P	−23.6, $^{3}J_{P,H}$ = 7.6 Hz	21.7, $^{3}J_{P,H}$ = 12.1 Hz	39.5, $^{3}J_{P,H}$ = 13.3 Hz	30.6, $^{3}J_{P,H}$ = 12.7 Hz, $^{1}J_{Se,P}$ = 740.0 Hz
^{1}H	1.80, s, 9H, C_4H_9	1.76 s, 9H, C_4H_9	1.72 s, 9H, C_4H_9	1.72 s, 9H, C_4H_9
^{13}C{^{1}H}	144.5, $^{1}J_{P,C}$ = 8.7 Hz, C^2	139.4, $^{1}J_{P,C}$ = 147.7 Hz, C^2	138.9, $^{1}J_{P,C}$ = 129.0 Hz, C^2	137.2, $^{1}J_{P,C}$ = 119.0 Hz, C^2
	129.3, $^{3+4}J_{P,C}$ = 2.3 Hz, C^5	127.5, $^{3+4'}J_{P,C}$ = 18.1 Hz, C^5	127.5, $^{3+4'}J_{P,C}$ = 18.0 Hz, C^5	127.7, $^{3+4'}J_{P,C}$ = 17.5 Hz, C^5
	120.0, $^{3+4}J_{P,C}$ = 1.9 Hz, C^4	120.8, $^{3+4}J_{P,C}$ = 3.2 Hz, C^4	122.4, $^{3+4}J_{P,C}$ = 2.5 Hz, C^4	122.8, $^{3+4}J_{P,C}$ = 2.3 Hz, C^4
	31.4, $^{4}J_{P,C}$ = 12.0 Hz, *t*-Bu-CH_3	30.3, *t*-Bu-CH_3	30.6, *t*-Bu-CH_3	30.8, *t*-Bu-CH_3
m.p.	124 °C	145 °C	174 °C	204 °C

Scheme 1. Synthesis of 1-*tert*-Butyl-2-diphenylphosphino-imidazole **2**

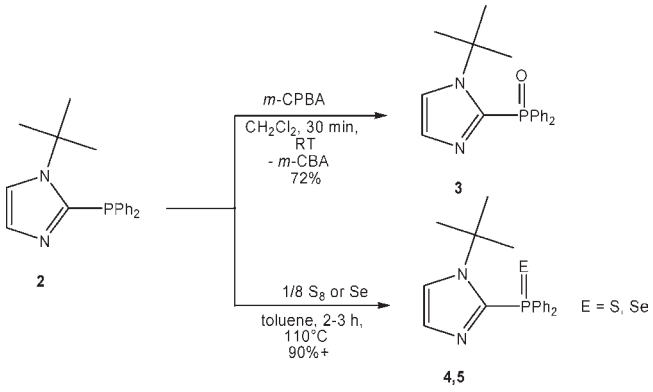


Reaction of 1-*tert*-Butyl-2-diphenylphosphino-imidazole (2) with *cis*-[Pt(PhCN)$_2$Cl$_2$] Complex. Ten milliliters of CH_2Cl_2 and 1-*tert*-butyl-2-diphenylphosphino-imidazole (**2**) (308 mg, 1 mmol) were placed in a Schlenk flask and *cis*-[Pt(PhCN)$_2$Cl$_2$] complex (472 mg, 1 mmol) was added, and the reaction mixture was heated at 40 °C for 3 h. The reaction was monitored using ^{31}P NMR. Observed products: **11**: −25.4 ($^{1}J_{Pt,P}$ = 3756.2 Hz), **12**: 10.9 ($^{1}J_{Pt,P}$ = 3898.6 Hz). Unfortunately, none of them could be crystallized or purified by column chromatography. Analysis: (**11**) ^{1}H NMR (300.1 MHz, CD_2Cl_2, 25 °C): δ = 7.30−7.23 (m, 10H, C_6H_5), 7.05 (d, $^{3}J_{H,H}$ = 1.13 Hz, 1H, C^5-H), 6.66 (d, $^{3}J_{H,H}$ = 1.13 Hz, 1H, C^4-H), 1.73 (s, 9H, C_4H_9); MS (ESI) data: exact mass calcd 538.0779 found 538.0818 (as $C_{19}H_{21}ClN_2PPt^+$); (**12**): exact mass calcd 846.2221 found 846.2222 (as $C_{38}H_{42}ClN_4P_2Pt^+$).

Results and Discussion

1-*tert*-butylimidazole (**1**) was subjected to metalation reactions using different bases and subsequent reaction with diphenylchlorophosphane; all reactions were monitored by ^{31}P NMR spectroscopy. The metalation reagents used were methyllithium, *n*-butyllithium, *tert*-butyllitium, lithium diisopropylamide, sodium bis(trimethylsilyl)amide, potassium *tert*-butoxide, and the combination of potassium *tert*-butoxide and *tert*-butyllithium (Lochmann-Schlosser superbase).[40] In most of the reactions of **1** the steric demand of the *tert*-butyl group caused kinetic problems, which led to the preferred formation of the following products, identified by their ^{31}P NMR shift (values given in brackets): tetraphenyldiphosphane (14.6 ppm),[41,42] or diphenylmethylphosphane (−26.3 ppm).[43] The formation of these products point to the reaction of unreacted metalation reagent with diphenylchlorophosphane. The 2-diphenylphosphino substituted imidazole derivative **2** was formed selectively with *tert*-butyllithium as base and diphenylchlorophosphane, and was isolated by crystallization (Scheme 1).

Scheme 2. Oxidation Reactions of (**2**) Using *m*-CPBA or Elemental Chalcogens (S_8 and Se)



It is interesting to note that all 2-diphenylphosphino substituted imidazole derivatives described in the literature so far have a ^{31}P{^{1}H} NMR resonance at around −30.0 ppm, unaffected by the nature of the N^1 substituent,[6,30−32,34,35] but in the case of **2** the phosphorus resonance was shifted to lower field (−23.6 ppm) (see Table 1); the signal showed a quintet in the proton-coupled spectrum due to a ^{3}J(P,H) coupling (7.6 Hz) to the *ortho*-phenyl protons. In the ^{13}C NMR spectrum all carbons except the *para*-phenyl carbon atoms exhibited couplings to the phosphorus atom. Whereas the coupling constants to the phenyl and the imidazole carbon atoms were in the expected range, the coupling to the carbon atoms of the *tert*-butyl methyl group was surprisingly large (12.0 Hz). Attempts to grow crystals suited for X-ray structure analysis always resulted in twinned crystals, and the structure of which could not be solved. Therefore, and to study the reactivity of **2**, various oxidation and complexation reactions were performed as described in Scheme 2.

The reactions of compound **2** with *meta*-chloroperbenzoic acid, elemental sulfur and selenium were quantitative according to ^{31}P NMR spectroscopy (see Scheme 2); the lower isolated yield of the phosphane oxide **3** was caused by the necessity to perform column chromatography to remove *meta*-chlorobenzoic acid. Elemental tellurium did not react with **2** under the same conditions. The products **4** and **5** crystallized out of the reaction mixtures and thus could easily be obtained in pure form; selected analytical data of compounds **2**, **3**−**5** are shown in Table 1. As expected for P^V derivatives the ^{31}P NMR signal of **3**−**5** was shifted to lower field compared to phosphane **2**, whereby the greatest shift was observed for the phosphane sulfide **4**. The same tendencies were observed before in the series of imidazole phosphane pnictogens.[32] In the ^{1}H NMR spectra the resonance signals for the aromatic protons were downfield shifted, whereas the signal for the *tert*-butyl methyl groups was upfield shifted. In the ^{13}C NMR spectra the magnitude of

(40) Ishikawa, T. *Superbases in Organic Synthesis*; John Wiley and Sons: West Sussex, 2009.
(41) Schmidpeter, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1985**, *22*, 323–325.
(42) Hunter, D.; Michie, J. K.; Miller, J. A.; Stewart, W. *Phosphorus, Sulfur Silicon Relat. Elem.* **1981**, *10*, 267–270.
(43) Moedritzer, K.; Maier, L.; Groenweghe, L. C. D. *J. Chem. Eng. Data* **1962**, *7*, 308–310.

the ^1J(P,C), ^3J(P,C), and ^4J(P,C) couplings to the aromatic carbons increased and the ^2J(P,C) coupling decreased, with respect to **2**. No coupling to the *tert*-butyl carbon atoms was observed. As usual, the magnitude of the ^1J(P,C) coupling was strongly influenced by the electronegativity of the pnictogens. Interestingly, the coupling to the C^5-carbon of the imidazole ring was much larger than the coupling to the imidazole C^4 carbon (18 Hz vs 2−3 Hz); in the (non-oxidized) **2**, both couplings were in the same range.

X-ray single-crystal structure analysis was performed for all three compounds **3**−**5**; crystals were obtained from diethyl ether solutions. All three compounds crystallized isostructural in the triclinic crystal system, space group $P\bar{1}$; for selected crystal data see Figure 1. Further information is provided in the Supporting Information section. Despite that the structures of **3**−**5** are the first reported of a diphenylphosphino substituted imidazole derivative, structural parameters shall not be discussed further as bond lengths and angles are in the common range for P^V chalcogenide derivatives.[44−46]

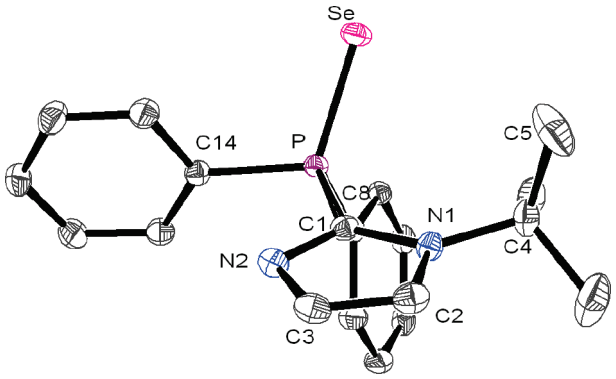
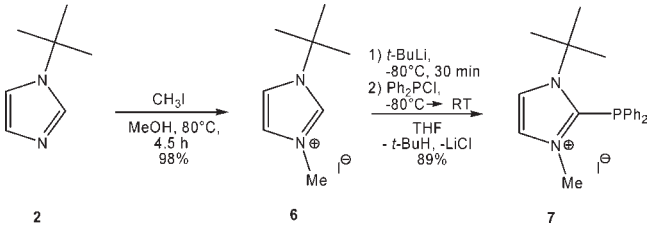


Figure 1. Molecular structure of **5** For details of the measurement see the Supporting Information section. Selected bond lengths [pm]: C1−N1 1.3837(19), C1−N2 1.3258(19), C2−C3 1.359(2), C4−N1 1.505(2), P−C1 1.8229(14), P−C8 1.8146(15), P−C14 1.8180(15), P−Se 2.1151(4).

Scheme 3. Synthesis of 1-*tert*-Butyl-2-diphenylphosphino-3-methylimidazolium Iodide (**7**)



A priori compound **2** possesses two basic centers, the N^3 nitrogen and the phosphorus, which might offer options to tune the reactivity via selective alkylation. To investigate this, the *N*-methylated product **7** was synthesized using 1-*tert*-butylimidazole (**1**), which was reacted with iodomethane in methanol to give the imidazolium salt **6**.[39] After metalation using *tert*-butyllithium and reaction with diphenylchlorophosphane, in analogy to the aforementioned reaction (see Scheme 3), the product **7** was obtained and purified by concentrating the reaction mixture in vacuo and removal of the byproduct; selected data are given in Table 2.

First test reactions on the alkylation of **2** using iodomethane in toluene showed the selective formation of only one product, having a ^{31}P NMR resonance at 18.8 ppm,[47] clearly indicating that the reaction exclusively occurred at the phosphorus atom. In agreement with the steric demand of the

Scheme 4. Reactions of **2** with $[W(CO)_5(thf)]$ and the Borane THF Complex

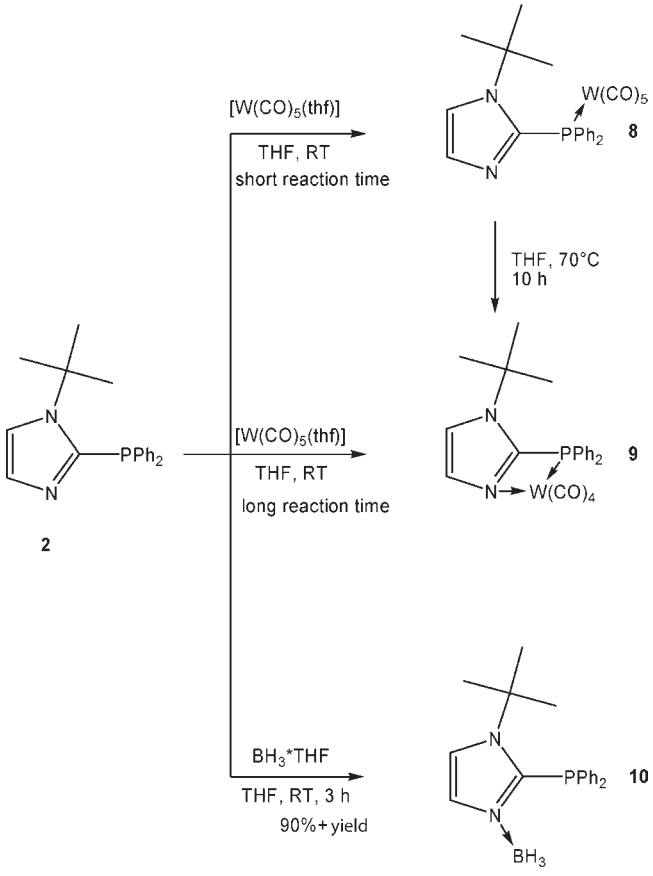
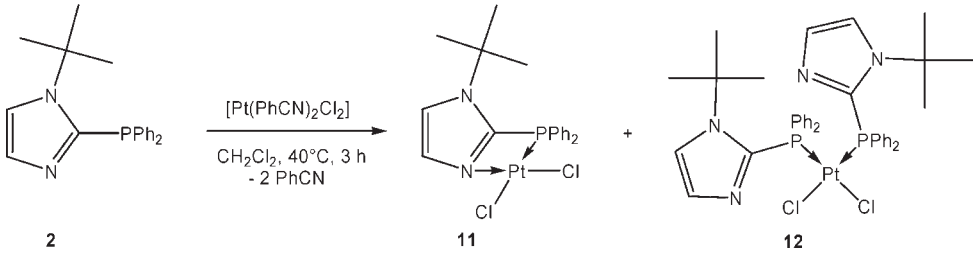


Table 2. Selected NMR Data (Chemical Shifts and Coupling Constants) and Melting Points of Compounds **7**, **8**, and **10**

analyt. data	**7**	**8**	**10**
^{31}P	−35.0, $^3J_{P,H}$ = 7.7 Hz	21.3, $^1J_{W,P}$ = 254.3 Hz	−19.5
^{1}H	3.75, s, 3H, N−CH_3		
	1.62, s, 9H, C_4H_9	0.67 s, 9H, C_4H_9	1.89 s, 9H, C_4H_9
			1.66, s br, 3 H, BH_3
$^{13}C\{^1H\}$		200.0, $^1J_{W,C}$ = 24.6 Hz, *trans*-CO	
		197.3, $^1J_{W,C}$ = 24.6 Hz, *cis*-CO	
	139.0, C^2	139.3, $^1J_{P,C}$ = 66.6 Hz, C^2	141.3, $^1J_{P,C}$ = 40.1 Hz, C^2
	128.4, $^{3+4}J_{P,C}$ = 6.5 Hz, C^5	129.9, $^{3+4}J_{P,C}$ = 1.9 Hz, C^5	131.7, $^{3+4}J_{P,C}$ = 5.2 Hz, C^5
	125.8, $^{3+4}J_{P,C}$ = 4.5 Hz, C^4	123.9, C^4	120.0, $^{3+4}J_{P,C}$ = 3.2 Hz, C^4
	34.9, $^4J_{P,C}$ = 10.0 Hz, N−CH_3		
	28.9, *t*-Bu-CH_3	30.2, *t*-Bu-CH_3	30.6, $^4J_{P,C}$ = 13.6 Hz, *t*-Bu-CH_3
m.p.	190 °C		130 °C

Scheme 5. Reaction of **2** with *cis*-$[Pt(PhCN)_2Cl_2]$ Complex



2 11 12

tert-butyl group in **2** the reaction was very slow, even at 110 °C and was not completed after 8 weeks (maximum conversion 50%); unfortunately, the product could not be isolated.

Aside from oxidation and alkylation reactions, the possible use of **2** as a ligand in coordination chemistry was tested, and, therefore, the reaction of **2** with $[W(CO)_5(thf)]$,[36] the borane-THF complex and *cis*-$[Pt(PhCN)_2Cl_2]$[48] was investigated (see Schemes 4 and 5). When **2** was reacted with $[W(CO)_5(thf)]$ at ambient temperature and the reaction stopped after a maximum time of 15 h, the light-yellow complex **8** was formed exclusively, showing a ^{31}P NMR resonance at 21.3 ppm with a $^1J(W,P)$ coupling of 254.3 Hz (for more data see Table 2). Surprisingly, the complex **8** was not stable in solution, and attempts to purify it via column chromatography failed. Complex **8** decomposed into the starting materials and the brown-yellow product **9** having a resonance at 14.4 ppm with a $^1J(W,P)$ coupling of 193.3 Hz. Heating a THF solution of **8** also resulted in the formation of complex **9**. The analytical data of the formed complexes is in good agreement with those reported by Yoshifuji et al. on 2-pyridylphosphine tungsten complexes[49] or Coles et al. on 1-aza-3-phospha-tungstacyclobut-1-enes.[50] Yoshifuji et al. did also observe an upfield shift combined with a decrease in the tungsten−phosphorus coupling constant when going from the pentacarbonyl to the tetracarbonyl chelate complex.

In addition, **9** shows four CO absorption bands in the IR spectrum, and three signals for the carbonyl groups in the ^{13}C NMR spectrum, typical for tungsten tetracarbonyl complexes. To the best of our knowlegde, compound **9** is only the fourth reported tetracarbonyl P,N-chelate tungsten complex, and just three tungsten complexes of diphenylphosphino substituted imidazole derivatives are literature known: one with κP-coordination (^{31}P NMR: $\delta = 17$) and two with κN-coordination (^{31}P NMR: $\delta = -31$ and -35).[51] Reacting **2** with the borane-THF complex yielded selectively product **10**, which was isolated by removing the solvent in vacuo and subsequent washing with *n*-pentane. Interestingly, the coordination of BH_3 exclusively occurred at the nitrogen atom (^{31}P NMR: $\delta = -19.5$); a P,B-coupling could not be determined (for more data see Table 2). The *N*-borane group was easily identified in the ^1H NMR spectra (1.66 ppm, s br), and the constitution was also established by mass spectrometric measurements (exact mass for $C_{19}H_{24}BN_2PNa^+$, found: 345.1669, calcd 345.1664). Complex **10** is a colorless solid melting at 130 °C. To the best of our knowledge, no examples of borane complexes, neither *P*- nor *N*-coordinated, of phosphorus substituted imidazole derivatives are known so far.

The formation of complex **9** increased our interest in the *cis*-chelating properties of **2**. Therefore, we studied the reaction of **2** with *cis*-$[Pt(PhCN)_2Cl_2]$ complex in dichloromethane, which yielded the two products **11** and **12** (ratio 3:1) having ^{31}P NMR resonances at −25.4 and 10.9 ppm, respectively, and $^1J(Pt,P)$ coupling constants of 3756.2 and 3898.6 Hz. Unfortunately, both compounds could not be separated via column chromatography or crystallization. Nevertheless, it can be safely assumed that a mixture of the *cis*-chelate **11** and complex **12** having two *P*-ligands was formed as we obtained further evidence from electrospray ionization (ESI) mass spectrometry, which showed molecular ion peaks with a mass-charge ratio of 538.0818 for **11** ($C_{19}H_{21}ClN_2PPt^+$, calcd: 538.0779) and a mass-charge ratio of 846.2222 for **12** ($C_{38}H_{42}ClN_4P_2Pt^+$, calcd: 846.2221).

Comparison of **11** and **12** with literature-known platinum complexes revealed that the complex [bis{2-{bis(1,1-dimethylethyl)phosphino-κP}-1-methyl-1*H*-imidazole}platinum(0)][52] is characterized by a ^{31}P resonance at 55.7 ppm and a $^1J(Pt,P)$ coupling constant of 4247.1 Hz, whereas the platinum(II) hydride complex having one bis(1,1-dimethylethyl)phosphino-κP ligand (coordinated via the phosphorus center) and the second ligand forming a four-membered chelate (via phosphorus and nitrogen coordination) has different NMR data (^{31}P NMR: $\delta = 52.6$, $^1J(Pt,P) = 2940.3$ Hz; $\delta = 39.4$, $^1J(Pt,P) = 2341.2$ Hz, $^2J(P,P) = 327.8$ Hz).[36] Because the first example has a Pt^0 center, the ^{31}P NMR data are not straightforwardly comparable, but it is known that, in general,

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formation of a chelate complex leads to a decrease of the ^{1}J(Pt,P) coupling constant magnitude.[52]

Conclusions

Metalation of 1-*tert*-butylimidazole (**1**) was successfully accomplished with *tert*-butyllithium, and the subsequent reaction with diphenylchlorophosphane yielded the C^2 substituted product **2**, whereas other bases predominantly yielded side-reaction products. The reactivity of **2** toward oxidation, alkylation, and complexation reactions was studied. Oxidation occurred selectively to yield the corresponding P^V-E products (E = O, S, Se) **3**−**5**, as firmly established by their X-ray crystal structures; derivatives **3**−**5** represent the first examples within the series of *P*-substituted imidazole derivatives. The influence of the sterical demanding *tert*-butyl group became apparent in the reaction of **2** with the borane-THF complex, which led to the first example of an *N*-coordinated phosphorus-containing imidazole derivative **10** (instead of the anticipated *P*-coordination). First studies on the ligating properties of **2** toward transition metals reveals that the formation of four-membered chelate κP- and κN-complexes tungsten and platinum complexes is preferred over *end-on* coordination, which might be preferred because of steric repulsion between the *N*-tert-butyl group and the C^2-bound phosphanyl substituent.

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Supporting Information Available: Refinement details of the X-ray crystal structure analysis of **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org. The data is also deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition numbers 778496, 778497, and 778498.