ORGANOMETALLICS

New Lithium Phosphonium Diylides: A Methylene and a Cyclopentadienyl Moiety as Ylidic Coordination Sites

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Supporting Information

ABSTRACT: A set of lithium phosphonium diylides Li[CH₂-PR₂-Cp^X] (9–12; Cp^X = C₅Me₄, C₅H₃tBu, R = Ph, Me) is presented. Two of the lithium complexes were characterized by means of single-crystal X-ray analysis, revealing a dimeric head-to-tail arrangement in the solid state. The coordination behavior of 9–12 in the liquid phase is solvent dependent. These lithium phosphonium diylides exist as contact ion pairs



in benzene and as solvent-separated ion pairs in THF solutions. Phosphonium salts $[H_3C-PR_2-Cp^XH)]^+I^-(1-4)$ are starting materials for the syntheses of the title compounds and exist as mixtures of isomers due to [1,5]-prototropic rearrangements. The dynamic behavior in solution has been investigated. Two different routes allow access to title compounds 9-12. Reactions of 1-4 with 2 equiv of *n*BuLi give 9-12 in a one-pot synthesis. In an alternative two-step route, dehydrodehalogenation of 1-4 with KH gives the corresponding phosphonium ylides 5-8. Two of these phosphonium ylides were characterized by single-crystal X-ray analysis. In one case two different conformers were obtained.

INTRODUCTION

Phosphonium diylides have a longstanding tradition as monoanionic, bidentate ligands in organometallic chemistry (Scheme 1, A).¹ Complexes of this versatile ligand system with

Scheme 1. Set of Isoelectronic, Monoanionic, Bidentate Phosphonium Diylide Ligands: Classical (A), Cp Substituted (CpPC Type Ligand, B), and bis-Cp Substituted (C) (R = Alkyl, Aryl)



metals across the entire periodic table have been studied² covering a broad spectrum of research interests, such as metal metal interactions,³ the development of pharmaceuticals,⁴ new synthetic methods in organic chemistry,⁵ and catalytic applications.^{3a,f,6} Within this field, polynuclear gold complexes in particular have to be mentioned. This class of compounds is sufficiently stabilized by type **A** ligands, and their characteristics and reactivity have been investigated.^{3a-f,7}

Not only the classical phosphonium diylides themselves have received considerable scientific interest but also a set of phosphonium-bridged *ansa*-metallocene ligands, which are formally derived thereof (Scheme 1, C). Main-group and transition-metal complexes based on type C ligands have been prepared and in some cases applied successfully as catalysts or as substrates in polymerization reactions.⁸ From an academic

point of view, type C ligands also allowed for the first structural characterization of a noncoordinated phosphonium diylide.⁹ In sharp contrast to the plethora of literature on organometallic compounds with phosphonium diylide ligands of types A and C, the hybrid ligand system of type B (CpPC ligand, Scheme 1) has scarcely been investigated. In fact, there is only a single publication on this kind of ligand system.¹⁰ The authors reported on type B phosphonium diylide (CpPC) complexes of sodium, in which the ligand system had an indenyl group instead of a Cp moiety and electron-withdrawing substituents attached to the second ylide functionality. Due to its electron-poor nature, the second ylide moiety does not interact with the metal center in the only structurally authenticated example.

Herein, we report the synthesis and characterization of a series of lithiated CpPC ligands, which bear an unsubstituted methylene functionality, keeping their metal coordinating character intact.

RESULTS AND DISCUSSION

The desired CpPC ligand systems can be derived from cyclopentadienyl-substituted phosphanes in a straightforward protocol. A variety of this small class of compounds is accessible with different substitution patterns both at the phosphorus atom and at the cyclopentadienyl moiety.¹¹ This allows for tuning of the electronic and steric parameters of the future ligand system.

Phosphonium Salts. Four phosphanes were chosen as representative starting materials (R_2P - Cp^X : R = Me, Ph, $Cp^X = C_5HMe_4$, C_5H_4tBu). Quaternization of these phosphanes with

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methyl iodide leads to the phosphonium salts 1-4 in good yields (Scheme 2). They exist as a mixture of isomers due to

Scheme 2. Synthesis of Cp-Substituted Phosphonium Salts, Which Exist as Mixtures of Isomers: 1, $R^1 = Ph$, R^2 , $R^3 = Me$; 2, R^1 , R^2 , $R^3 = Me$; 3, $R^1 = Ph$, $R^2 = H$, $R^3 = tBu$; 4, $R^1 = Me$, $R^2 = H$, $R^3 = tBu$



[1,5]-prototropic rearrangements. These isomerization processes were investigated by means of NMR spectroscopy (for details see the Supporting Information):

Phosphonium Ylides. Dehydrodehalogenation of phosphonium salts 1-4 with potassium hydride gives the phosphonium ylides 5-8 (Scheme 3, left).¹² Two conformers

Scheme 3. Two-Step (Left and Bottom) and One-Pot Syntheses (Right) of a Series of Lithium Phosphonium Divlides (9–12)



of 5 (5a and 5b) and 6 have been characterized by means of single-crystal X-ray analysis (Figure 1). In compound 5, there is one major structural difference between the two modifications 5a and 5b: the torsion angle C2-C1-P1-C10/11/17 reaches its minimum for C17 (which is part of a phenyl substituent) in the case of **5a** and for C10 (which is part of a methyl group) in the case of **5b**. **6** crystallizes with two chemically equivalent but crystallographically independent molecules in the asymmetric unit. The P-C^{Cp} bonds in **5a**,**b** and **6** can be described by significant contributions of both the ylide and the ylene resonance structure.¹³ This is in agreement with earlier reports on comparable systems¹⁴ and can be supported by two structural parameters. (i) The $P-C^{Cp}$ bonds (1.717(2)-1.735(3) Å) are significantly longer than the corresponding bonds in nonstabilized phosphonium ylides (e.g., 1.661 Å in $Ph_3P=CH_3$ ¹⁵ but considerably shorter than P-C single bonds.¹⁶ (ii) Within the cyclopentadienyl substituent there are two long, one medium, and two short C-C bond distances, all of which range between values known for single and double C-C bonds.¹⁷

Phosphonium Divlides. Deprotonation of the vlides 5-8 gives the desired CpPC ligands. However, the formation of detectable amounts of alkali-metal phosphonium divlides was not observed when 5-8 were exposed to excess potassium hydride and long reaction times were applied. In contrast, the only so far fully characterized complex with a CpPC type ligand is accessible by deprotonation of the corresponding ylide with an alkali-metal hydride. This reveals the higher acidity of this formerly reported ylide in comparison to 5-8. In turn, CpPC ligands derived from 5-8 can be expected to show a stronger electron-donating character. Reaction of 5-8 with the strong base nBuLi allowed for the synthesis of lithium phosphonium divides 9-12 (Scheme 3, bottom). These compounds can also be obtained from phosphonium salts 1-4 in a one-pot reaction which combines a dehydrodehalogenation and a deprotonative metalation (Scheme 3, right).

Compounds 9-12 are readily soluble in THF, diethyl ether, or benzene and modestly soluble in pentane or hexane.



Figure 1. Molecular structures of **5** (**5a**, left; **5b**, middle) and **6** (right). There are two crystallographically independent but chemically equivalent molecules in the asymmetric unit of **6**. One of them shows a crystallographic disorder in the PMe₃ unit and is not displayed. Structural parameters of motifs analogous to those of the molecule displayed above are given in parentheses. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) are as follows. **5a**: P1–C1, 1.720(2); P1–C10, 1.797(3); P1–C11, 1.815(3); P1–C17, 1.807(2); C1–C2, 1.439(4); C2–C3, 1.394(4); C3–C4, 1.420(4); C4–C5, 1.378(4); C5–C1, 1.443(4); C1–C2–C3, 106.8(2); C2–C3–C4, 109.1(2); C3–C4–C5, 109.1(2); C4–C5–C1, 107.4(2); C5–C1–C2, 107.6(2); C17–P1–C1–C2, 17.6(3); C17–P1–C1–C5, 176.5(2). **5b**: P1–C1, 1.717(2); P1–C10, 1.791(2); P1–C11, 1.815(2); P1–C17, 1.810(2); C1–C2, 1.448(3); C2–C3, 1.375(3); C3–C4, 1.432(3); C4–C5, 1.376(3); C5–C1, 1.440(3); C1–C2–C3, 107.1(2); C2–C3–C4, 109.4(2); C3–C4–C5, 108.5(2); C4–C5–C1, 107.8(2); C5–C1–C2, 107.3(2); C10–P1–C1–C2, 5.8(2); C10–P1–C1–C5–C9, 177.4(2). **6**: P1–C1, 1.725(3) (1.735(3)); P1–C10, 1.816(4) (1.780(26)); P1–C11, 1.773(4) (1.749(19)); P1–C17, 1.774(4) (1.804(26)); C1–C2, 1.433(4) (1.436(4)); C2–C3, 1.389(4) (1.395(4)); C3–C4, 1.418(4) (1.421(4)); C4–C5, 1.388(4) (1.399(3)); C5–C1, 1.444(4) (1.441(4)); C1–C2–C3, 107.6(2) (107.8(2)); C2–C3–C4, 109.0(2) (108.6(2)); C3–C4–C5 108.7(2) (108.6(2)); C4–C5–C1, 107.5(2) (108.0(2)); C5–C1–C2, 107.2(2) (107.0(2)); C10–P1–C1–C2, 3.4(3) (23.5(9)); C10–P1–C1–C5, 177.7(2) (161.8(8)).

Interactions of the CpPC ligands in 9–12 with the metal center have been investigated in solution. The methylene group and the cyclopentadienyl moiety in each of these ligands are the donor sites which might interact with the alkali metal. Whereas no close Li–C(methylene) or Li–Cp^X (Cp^X = C₃Me₄ for 9 and 10; Cp^X = C₃H₃tBu for 11 and 12) contacts were detected in solutions of 9–12 in the polar solvent THF, both functionalities show interactions with Li centers in solutions of 9–12 in the nonpolar solvent benzene. Interactions of the methylene functionality with the lithium center were studied by ¹³C NMR spectroscopy. In absence of Li–C(methylene) interactions, the methylene carbon atom gives rise to a doublet in the ¹³C NMR spectrum due to ¹J_{CP} coupling. Indeed, a signal with the expected multiplicity is observed in ¹³C NMR spectra of THF solutions of 9–12 (Figure 2 (left) for 9 as a



Figure 2. Signals in ¹³C NMR spectra due to carbon atom of the methylene moiety of 9 in THF- d_8 (doublet, left) and C_6D_6 (broad signal, right).

representative example). In the case of Li–C(methylene) contacts, the methylene carbon atom in **9–12** theoretically gives rise to a doublet of triplets overlapped by a doublet of quartets in the ¹³C NMR spectrum due to the presence of ³¹P $(I = \frac{1}{2}, N = 100\%)$, ⁶Li (I = 1, N = 7.4%), and ⁷Li nuclei $(I = \frac{3}{2}, N = 92.6\%)$. In fact, the multiplet is not fully resolved and a broad signal is observed for the methylene carbon atom in ¹³C NMR spectra of C₆D₆ solutions of **9–12**, providing evidence of interactions between the methylene moiety and the metal center (Figure 2 (right) for **9** as a representative example).

Interaction of the Cp^X moieties with Li centers was studied by ⁷Li NMR spectroscopy according to the method established by Cox et al.¹⁸ High-field ⁷Li NMR chemical shifts for lithium cyclopentadienyl compounds are indicative of contact ion pairs to be formed, whereas low-field chemical shifts prove the presence of solvent-separated ion pairs (see reference data for LiCp in Table 1). The data for 9-12 provide evidence of contact ion pairs formed in noncoordinating solvents such as pentane and benzene and separated ion pairs present in the

Table 1. Solvent Dependence of Chemical Shift in ⁷Li NMR Spectra of LiCp (Cox et al.)¹⁸ and 9-12 (This Work)

		chem shift (⁷ Li NMR)/ppm			
compd	pentane	benzene	THF	HMPT ^a	
9	-5.20	-5.54	-0.89		
10	-5.92	-6.36	1.11		
11	-5.98	-5.89	0.92		
12	-6.62	-7.02	-2.39		
LiCp			-8.37	-0.88	
	OD(M)				

 a HMPT = OP(NMe₂)₃.

coordinating solvent THF (Table 1). Solvent-separated ion pairs of phosphonium diylides in solution (and in the solid state) have been reported previously for complexes of calcium and barium, which have a higher tendency than lithium to form ionic structures.⁹ However, detailed studies concerning C–Li bonding of type **A** or **C** lithium phosphonium diylides (Scheme 1) in solution have not been reported so far.^{1b,8c} Thus, this is the first study providing a more profound insight into the metal–ligand interactions of lithium phosphonium diylides in solution.¹⁹

Lithium complexes of phosphonium divlides have been known since the early days of this class of compounds and have been used as transmetalation reagents ever since.^{1a,20} However, they have eluded structural characterization for more than three decades.²¹ Only three such compounds have been analyzed by means of single-crystal X-ray analysis to date.^{21,22} Single crystals of compounds 9 and 11 were obtained from solutions in pentane and hexane, respectively, at lowered temperatures. They both crystallize in the triclinic space group $P\overline{1}$ with two crystallographically independent formula units per asymmetric unit. The molecular structures of the two compounds exhibit similar structural parameters and will be discussed together. 9 and 11 both form dimers with a head-to-tail arrangement in the solid state (Figure 3).²³ The lithium atoms in 9 and 11 are coordinated by an η^{5} -Cp moiety and a methylene group. No donor solvent molecules are bound to the Li centers, which underlines the good electron-donating character of the two ylidic coordination sites in the CpPC ligand system.²⁴ Cp^{centroid}-Li-C bond angles range from 163.8(1) to 173.5(2)°. The slight bending was ascribed to geometric constraints dictated by the dimeric arrangement. The Li-C(methylene) bonds of 2.091(3)-2.112(3) Å are marginally shortened in comparison to the corresponding bonds in the other three crystallographically characterized lithium phosphonium divlides.^{21,22} This was ascribed to the fact that further neutral donor ligands are attached to the metal center in the latter cases. The Li-Cp^{centroid} distances range from 1.847(2) to 1.866(2) Å (in the case of 9) and from 1.880(4) to 1.912(3) Å (in the case of 11). The stronger electron-donating character of the C_5Me_4 fragment and the higher steric bulk of the C_5H_3tBu moiety explain the shorter Li-Cp^{centroid} distances in the former case. All these values are in the range of known Li-Cp^{centroid} distances in lithium complexes with an η^5 -Cp motif.²⁵ The C-C bond lengths in the Cp fragments in 9 and 11 are between values expected for single and double bonds, indicating the presence of a delocalized π -electron system. All phosphorus atoms in these compounds are found in a distorted-tetrahedral coordination geometry $(C-P-C, 102.9(1)-116.0(1)^\circ)$. Compounds 9 and 11 represent lithium cyclopentadienyl derivatives with an additional neutral coordination site attached to the Cp fragment. Complexes known in the literature which also belong to this small class of compounds usually form oligomeric structures in the solid state.²⁶ Thus, a dimeric arrangement as observed in the case of 9 and 11 is unprecedented for such compounds. In comparison to other lithium phosphonium divlides, it is remarkable that 9 and 11 can be obtained without additional neutral ligands bound to the metal center.^{21,22}

Preliminary reactivity studies concerning transmetalation reactions of the CpPC ligand are promising. Reaction of **9** with CuCl gives the analogous copper complex Cu[CH₂-PPh₂-C₅Me₄)] (13), which was characterized spectroscopically (Scheme 4).²⁷ The full potency of transmetalation reactions

Article



Figure 3. Dimeric arrangements in molecular structures of **9** (left) and **11** (right). There are two crystallographically independent but chemically equivalent molecules in the asymmetric unit of **9**, only one of which is displayed (structural parameters of analogous motifs are given in parentheses). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) are as follows. **9**: Li1–Cp^{centroid}, 1.866(2) (1.847(2)); Li1–C10', 2.112(3) (2.091(3)); P1–C1, 1.762(2) (1.768(3)); P1–C10, 1.724(2) (1.726(2)); P1–C11, 1.825(1) (1.820(1)); P1–C17, 1.809(1) (1.819(2)); C1–C2, 1.439(2) (1.436(2)); C2–C3, 1.397(2) (1.406(2)); C3–C4, 1.421(2) (1.416(2)); C4–C5, 1.404(2) (1.399(2)); C1–C5, 1.441(2) (1.441(2)); Cp^{entroid}–Li1–C10', 167.7(1) (163.8(1)); C1–P1–C10, 114.7(7) (113.0(1)); C1–P1–C17, 104.9(1) (106.0(1)); C1–P1–C17, 111.2(1) (112.0(1)); C10–P1–C11, 116.0(1) (115.7(1)); C10–P1–C17, 104.7(1) (105.8(1)); C11–P1–C17, 104.9(1) (104.3(1)). **11**: Li1–Cp^{entroid}, 1.880(4); Li1–C44, 2.099(4); P1–C1, 1.774(2); P1–C10, 1.811(2); P1–C16, 1.824(2); P1–C22, 1.708(3); C1–C2, 1.411(3); C2–C3, 1.402(3); C3–C4, 1.405(3); C4–C5, 1.392(3); C1–C5, 1.419(3); C24–C25, 1.401(3); C25–C26, 1.419(3); C26–C27, 1.397(3); C23–C27, 1.417(3); Cp^{entroid}–Li1–C44, 172.5(2); C1–P1–C10, 107.6(1); C1–P1–C16, 106.8(1); C1–P1–C22, 112.1(1); C10–P1–C16, 102.9(1); C10–P1–C22, 111.6(1); C16–P1–C22, 115.2(1); Cp^{entroid}–Li2–C22, 165.2(2); C23–P2–C38, 106.7(1); C32–P2–C44, 112.6(1); C32–P2–C38, 103.7(1); C32–P2–C44, 114.8(1); C38–P2–C44, 110.1(1).

with the CpPC ligand system is currently being exploited in our laboratories.



^aWe suggest a dimeric arrangement of this complex in the solid state.²⁷

CONCLUSION

A series of monoanionic, bidentate phosphonium diylide ligands with a methylene and a cyclopentadienyl group as coordination sites (CpPC ligands) is reported. The lithium complexes Li[CH₂-PR₂-Cp^X] (**9–12**: Cp^X = C₅Me₄, C₅H₃*t*Bu; R = Ph, Me) are accessible in a one-pot synthesis from the corresponding phosphonium iodides **1–4**. The phosphonium salts **1–4** exist as mixtures of isomers due to [1,5]-prototropic rearrangements. **9–12** are also accessible in a two-step synthesis from **1–4**. The products of the first step, phosphonium ylides **5–8**, have been isolated and characterized, two of them by means of single crystal X-ray analysis. Two conformers of one of the phosphonium ylides were obtained. Single-crystal X-ray analysis of lithium complexes **9** and **11** revealed a dimeric head-to-tail arrangement. In contrast to the only other fully characterized CpPC complex,¹⁰ both coordination sites in **9** and **11** interact with the metal center. The coordination properties of the CpPC ligands in solution are solvent dependent. Whereas no close interactions with the metal center were found in solutions of the coordinating solvent THF, the methylene and the cyclopentadienyl moiety interact with the alkali metal in solutions of the weakly coordinating solvent benzene.

EXPERIMENTAL SECTION

General Remarks. All experimental procedures were carried out under an atmosphere of purified argon or nitrogen using standard Schlenk techniques or a glovebox. The solvents used were dried and degassed according to standard protocols. Chemicals were purchased from Alfa Aesar or Aldrich and used without further purification. 6 was synthesized according to the literature.²⁸ NMR measurements were performed using a Bruker DPX 250, AVANCE 300, DRX 400, or DRX 500 spectrometer at 25 °C. The chemical shifts of ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and are reported relative to the chemical shift of tetramethylsilane. The resonances in ¹H and ¹³C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HMQC, HMBC). The ⁷Li and ³¹P NMR resonances are reported relative to external standards, an aqueous solution of LiCl and phosphoric acid (85%), respectively. Elemental analyses were carried out at the Analytical Laboratory of the Department of Chemistry/ Philipps-Universität Marburg. EI mass spectra were recorded using a Finnigan MAT CH7 instrument (E = 70 eV). ATR FT IR spectra were obtained using a Bruker Alpha-P spectrometer. For details concerning the synthesis of phosphonium salts 1-4 see the Supporting Information.

Phosphonium Ylides 5, 7, and 8. The phosphonium salt (1, 3.90 g, 8.70 mmol; 3, 1.10 g, 2.47 mmol; 4, 6.50 g, 20.0 mmol) was suspended in THF (40–180 mL), and KH (in the case of 1, 0.484 g, 12.1 mmol; in the case of 3, 0.136 g, 3.39 mmol; in the case of 4, 1.14

g, 28.4 mmol) was added. The liquid phase subsequently turned yellow. After 2 days the reaction mixture was filtered and the residue was washed with diethyl ether $(3 \times 5 \text{ mL})$. All volatiles were removed from the filtrate to give a yellow (in the case of 5), beige (in the case of 7), or colorless solid (in the case of 8). 7 was recrystallized from THF solution at -30 °C. Yield: 5, 2.57 g, 8.01 mmol, 92%; 7, 0.628 g, 1.96 mmol, 79%; 8, 3.28 g, 16.7 mmol, 82%.

 $MePh_2PC_5Me_4$ (5). ¹H NMR (300.1 MHz, C_6D_6): δ 1.70 (d, ² J_{HP} = 12.8 Hz, 3H, PMe), 2.10 (s, 6H, 2,5-CpMe2), 2.49 (s, 6H, 3,4-CpMe2), 6.91-6.96 (m, 4H, o-/m-Ph), 6.99-7.04 (m, 2H, p-Ph), 7.28-7.35 (m, 4H, *m*-/*o*-Ph) ppm. ¹H NMR (300.1 MHz, THF- d_8): δ 1.70 (s, 6H, 2,5-Cp Me_2), 1.88 (s, 6H, 3,4-Cp Me_2), 2.34 (d, ${}^2J_{HP}$ = 13.1 Hz, 3H, PMe), 7.45-7.49 (m, 4H, o-Ph), 7.52-7.55 (m, 2H, p-Ph) 7.57-7.64 (m, 4H, *m*-Ph) ppm. ¹H NMR (300.1 MHz, Py- d_5): δ 1.99 (s, 6H, $2,5-/3,4-CpMe_2$, 2.26 (s, 6H, 3,4-/2,5-CpMe_2), 2.36 (d, ${}^{2}J_{HP} = 13.0$ Hz, 3H,PMe), 7.35-7.40 (m, 4H, o-/m-Ph), 7.46-7.50 (m, 2H, p-Ph), 7.66–7.72 (m, 4H, m-/o-Ph) ppm. ¹³C NMR (75.5 MHz, $C_6 D_6$): δ 12.2 (ii) 41, 41, m/0-11) ppn. C NMR (73.5 MR, C_6D_6). 0 12.2 (s, 3,4-CpMe₂), 14.5 (s, 2,5-CpMe₂), 15.2 (d, ${}^{1}J_{CP} = 61.4$ Hz, PMe), 68.4 (d, ${}^{1}J_{CP} = 111.4$ Hz, 1-Cp), 119.2 (d, ${}^{2}J_{CP} = 15.5$ Hz, 2,5-Cp), 121.4 (d, ${}^{3}J_{CP} = 18.4$ Hz, 3,4-Cp), 128.8 (d, ${}^{2/3}J_{CP} = 11.8$ Hz, o-/ m-Ph), 130.7 (d, ${}^{1}J_{CP} = 130.7$ Hz, ipso-Ph), 131.7 (d, ${}^{4}J_{CP} = 2.7$ Hz, p-Ph), 132.8 (d, ${}^{3/2}J_{CP} = 10.2$ Hz, m-/o-Ph) ppm. ${}^{13}C$ NMR (1000) MULTING (d) 5.14 (d, 44.2) (d, 2.5) MHz, THF- d_8): δ 11.6 (d, ${}^{4}J_{CP}$ = 2.8 Hz, 3,4-CpMe₂), 14.9 (s, 2,5-CpMe₂), 15.2 (d, ${}^{1}J_{CP} = 61.6$ Hz, PMe), 69.1 (d, ${}^{1}J_{CP} = 111.0$ Hz, 1-Cp), 118.8 (d, ${}^{2}J_{CP} = 15.2$ Hz, 2,5-Cp), 120.1 (d, ${}^{3}J_{CP} = 18.4$ Hz, 3,4-Cp), 129.4 (d, ${}^{2/3}J_{CP} = 11.7$ Hz, o-/m-Ph), 131.4 (d, ${}^{1}J_{CP} = 83.9$ Hz, (cp), 123.4 (d, $J_{CP} = 11.7$ Hz, p-Ph), 133.4 (d, ${}^{3/2}J_{CP} = 10.3$ Hz, m-/ *o*-Ph) ppm. ³¹P NMR (121.5 MHz, C_6D_6): δ 2.1 ppm. ³¹P NMR (121.5 MHz, THF- d_8): δ 2.8 ppm. ³¹P NMR (121.5 MHz, Py- d_5): δ 3.2 ppm. Anal. Calcd for C₂₂H₂₅P (320.41 g/mol): C, 82.47; H, 7.86. Found: C, 81.98; H, 8.25. EI/MS (70 eV): m/z (%) 320 (43) [M⁺], 305 (18) $[(M - Me)^+]$, 281 (100). HR-EI/MS (70 eV): m/z (%) 320.1686 (56) [M⁺⁺]. IR: 2939 (w), 2900 (m), 2845 (m), 1435 (s), 1278 (s), 1151 (m), 1103 (m), 1027 (m), 997 (m), 889 (s), 751 (s), 741 (s), 692 (s), 510 (s), 487 (s), 465 (s), 453 (s) cm⁻¹

 $MePh_2PC_5H_3tBu$ (7). ¹H NMR (300.1 MHz, CDCl₃): δ 1.29 (s, 9H, tBu), 2.56 (d, ${}^{2}J_{\rm HP}$ = 12.0 Hz, 3H, PMe), 6.10–6.09 (m, 2H, 4,5-C₅H₃tBu), 6.31(m, 1H, 2-C₅H₃tBu), 7.64–7.55 (m, 10H, PPh₂) ppm. ¹H NMR (300.1 MHz, C_6D_6): δ 1.67 (s, 9H, tBu), 1.76 (d, ²J_{HP} = 15.0 Hz, 3H, PMe), 6.38-6.43 (m, 2H, C₅H₃tBu), 7.35-6.85 (m, 10H, PPh₂; 1H, C₅H₃tBu) ppm. ¹H NMR (400.1 MHz, THF-d₈): δ 1.21 (s, 9H, tBu), 2.33 (d, ${}^{2}J_{HP}$ = 12.0 Hz, 3H, PMe), 5.76-5.91 (m, 2H, C₅H₃tBu), 6.07 (m, 1H, C₅H₃tBu), 7.24-7.66 (m, 10H, PPh₂) ppm. ¹³C NMR (75.5 MHz, CDCl₃): δ 12.5 (d, ¹ J_{CP} = 62.2 Hz, PMe). 30.7 (s, $C(CH_3)_3$), 32.5 (s, $C(CH_3)_3$), 80.2 (d, ${}^1J_{CP}$ = 118.9 Hz, 1- $C_{\rm 5}H_{3}tBu$), 109.2 (d, ${}^{2}J_{\rm CP}$ = 14.9 Hz, 2- $C_{\rm 5}H_{3}tBu$), 110.3 (d, ${}^{3}J_{\rm CP}$ = 15.5 Hz, $4-C_{\rm S}H_{3}Hd$, 10.5.2 (d, ${}^{1}J_{\rm CP} = 11.9$ Hz, $2-C_{\rm S}H_{3}Hd$), 110.5 (d, ${}^{1}J_{\rm CP} = 12.9$ Hz, $4-C_{\rm S}H_{3}tBu$), 113.6 (d, ${}^{2}J_{\rm CP} = 14.4$ Hz, $5-C_{\rm S}H_{3}tBu$), 125.7 (d, ${}^{1}J_{\rm CP} = 89.4$ Hz, *ipso*-Ph), 129.2 (d, ${}^{2}J_{\rm CP} = 12.4$ Hz, *o*-Ph), 132.5 (d, ${}^{3}J_{\rm CP} = 10.6$ Hz, *m*-Ph), 133.2 (d, ${}^{4}J_{\rm CP} = 2.8$ Hz, *p*-Ph), 142.4 (d, ${}^{3}J_{\rm CP} = 15.3$ Hz, 3-2 $C_{5}H_{3}tBu$) ppm. ¹³C NMR (62.5 MHz, THF- d_{8}): δ 12.0 (d, ¹ J_{CP} = 62.5 Hz, PMe), 32.6 (s, $C(CH_3)_3$), 33.2 (s, $C(CH_3)_3$), 89.4 (d, ${}^{1}J_{CP} = 120.0$ Hz, 1-C₅H₃tBu), 107.9 (d, ${}^{2}J_{CP}$ = 15.0 Hz, 2-C₅H₃tBu), 109.4 (d, ${}^{3}J_{CP}$ = 16.3 Hz, $4-C_3H_3tBu$), 113.2 (d, ${}^2J_{CP} = 14.4$ Hz, $5-C_5H_3tBu$), 129.3 (d, ${}^4J_{CP} = 2.5$ Hz, p-Ph), 129.3 (d, ${}^3J_{CP} = 11.8$ Hz, m-Ph), 133.2 (d, ${}^2J_{CP} = 10.6$ Hz, o-Ph), 137.0 (d, ${}^3J_{CP} = 15.0$ Hz, $3-C_3H_3tBu$) ppm. A resonance due to the ipso-Ph carbon atoms was not detected. ³¹P NMR (121.5 MHz, $C_6 D_6^{-1}$): δ 4.46 ppm. ³¹P NMR (121.5 MHz, Et₂O): δ 5.79 ppm. ³¹P NMR (161.9 MHz, THF- d_8): δ 6.40 ppm. EI/MS: m/z (%) 320.2 (21%) [M⁺], 305.1 (100) [(M - CH₃)⁺]. IR: 2951 (w), 2896 (m), 1202 (m), 1090 (m), 880 (m), 740 (s), 689 (s), 666 (s), 530 (m), 499 (s), 465 (s), 450 (s) cm⁻¹.

$$\begin{split} &\textit{Me_3PC_5H_3tBu} \ (8). \ ^{1}\text{H} \ \text{NMR} \ (300.1 \ \text{MHz}, \ C_6D_6): \ \delta \ 0.72 \ (d, \ ^{2}J_{\text{HP}} = \\ & 13.2 \ \text{Hz}, \ 9\text{H}, \ \text{PMe_3}), \ 1.72 \ (s, \ 9\text{H}, \ tBu), \ 6.21 \ (m, \ 1\text{H}, \ C_5H_3t\text{Bu}), \ 6.37 \\ & (m, \ 1\text{H}, \ C_5H_3t\text{Bu}), \ 6.78 \ (m, \ 1\text{H}, \ C_5H_3t\text{Bu}) \ \text{ppm.} \ ^{1}\text{H} \ \text{NMR} \ (300.1 \ \text{MHz}, \ \text{THF-}d_8): \ \delta \ 1.19 \ (s, \ 9\text{H}, \ tBu), \ 1.69 \ (d, \ ^{2}J_{\text{HP}} = \ 13.6 \ \text{Hz}, \ 9\text{H}, \\ & \text{PMe_3}), \ 5.96-5.88 \ (m, \ 3\text{H}, \ C_5H_4t\text{Bu}) \ \text{ppm.} \ ^{13}\text{C} \ \text{NMR} \ (75.5 \ \text{MHz}, \\ & \text{C}_6D_6): \ \delta \ 13.2 \ (d, \ ^{1}J_{\text{CP}} = \ 59.6 \ \text{Hz}, \ \text{PMe_3}), \ 32.7 \ (d, \ ^{4}J_{\text{CP}} = \ 1.7 \ \text{Hz}, \\ & \text{C}(\text{CH}_3)_3), \ 33.6 \ (s, \ \text{C}(\text{CH}_3)_3), \ 79.2 \ (d, \ ^{1}J_{\text{CP}} = \ 113.3 \ \text{Hz}, \ 1-C_5\text{H}_3t\text{Bu}), \\ & 106.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.7 \ \text{Hz}, \ 4-C_5\text{H}_4t\text{Bu}), \ 111.7 \ (d, \ ^{2}J_{\text{CP}} = \ 17.9 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{H}_4t\text{Bu}), \ 141.1 \ (d, \ ^{3}J_{\text{CP}} = \ 16.2 \ \text{Hz}, \ 2-/5-C_5\text{Hz}, \ 14.5 \ \text{Hz}, \ 14.5 \ \text{Hz}$$

16.8 Hz, $3 \cdot C_5 H_4 tBu$) ppm. ³¹P NMR (121.5 MHz, $C_6 D_6$): δ -4.24 ppm. ³¹P NMR (121.5 MHz, THF- d_8): δ -2.19 ppm. EI/MS: m/z (%) 196 (24) [M]⁺, 181 (100) [(M - CH₃)⁺]. Anal. Calcd for C₁₂H₂₁P (196.27 g/mol): C, 73.43; H, 10.78. Found: C, 72.81; H, 10.31. IR: 2974 (m), 2943 (m), 2903 (m), 1290 (w), 1202 (m), 1176 (w), 1093 (m), 978 (m), 952 (m), 941 (m), 909 (m), 863 (w), 767 (s), 746 (w), 687 (w), 662 (s), 609 (w) cm⁻¹.

Phosphonium Diylides 9–12. *Method A.* A solution of the phosphonium ylide (5, 250 mg, 0.78 mmol; 6, 101 mg, 0.52 mmol; 7, 157 mg, 0.49 mmol; 8, 77 mg, 0.39 mmol) in diethyl ether (5 mL) was cooled to -78 °C and treated with a solution of *n*BuLi in hexane (1.6 M: in the case of 5, 485 μ L, 0.78 mmol; in the case of 6, 325 μ L, 0.52 mmol; in the case of 7, 305 μ L, 0.49 mmol; in the case of 8, 245 μ L, 0.39 mmol). After 1 h the reaction mixture was warmed to ambient temperature. All volatiles were removed under reduced pressure. The residue was suspended in pentane (10 mL), and the supernatant was decanted after centrifugation. The process was repeated. All volatiles were removed from the combined liquid phases under reduced pressure to give a beige solid, which was dried in vacuo. Yield: 9, 235 mg, 0.72 mmol, 92%; 10, 61 mg, 0.30 mmol, 58%; 11, 146 mg, 0.45 mmol, 91%; 12, 53 mg, 0.26 mmol, 67%.

Method B. A suspension of the phosphonium salt (1, 623 mg, 1.39 mmo; 2, 162 mg, 0.50 mmol; 3, 155 mg, 0.35 mmol; 4, 150 mg, 0.46 mmol) in diethyl ether (5–10 mL) was cooled to -78 °C. A solution of *n*BuLi in hexane (1.6 M: in the case of 1, 1.74 mL, 2.78 mmol; in the case of 2, 0.625 μ L, 1.0 mmol; in the case of 3, 440 μ L, 0.70 mmol; in the case of 4, 575 μ L, 0.46 mmol) was added. The reaction mixture was warmed to ambient temperature over a period of 2 h. All volatiles were removed under reduced pressure. The residue was suspended in pentane (10 mL), filtered, and washed with pentane (2 × 5 mL). All volatiles were removed from the combined liquid phases to give a beige solid, which was dried in vacuo. Yield: 9, 290 mg, 0.89 mmol, 64%; 10, 86 mg, 0.40 mmol, 87%; 11, 53 mg, 0.26 mmol, 67%; 12, 86 mg, 0.43 mmol, 93%.

In methods A and B, diethyl ether can be substituted for THF. In all cases the isolated compounds must be dried in vacuo for several hours or recrystallized from pentane to remove the last 1 equiv of the donor solvent molecule (Et_2O or THF).

 $[(Li-CH_2-PPh_2-C_5Me_4)_2]$ (9). ¹H NMR (300.1 MHz, C₆D₆): δ 0.15 (d, ${}^{2}J_{HP}$ = 11.4 Hz, 2H, PCH₂Li), 1.27–1.31 (m, 4H, β -THF), 1.89 (s, 6H, 3,4-CpMe₂), 2.29 (s, 6H, 2,5-CpMe₂), 3.79-3.83 (m, 4H, α -THF), 7.03 (br s, 6H, m-/o-,p-Ph), 7.62-7.67 (m, 4H, o-/m-Ph) ppm. ¹H NMR (400.0 MHz, THF- d_8): δ 0.08 (d, ² J_{HP} = 11.2 Hz, 2H, PCH₂), 1.57 (s, 6H, 3,4-CpMe₂), 1.75-1.79 (m, 4H, β-THF), 1.88 (s, 6H, 2,5-CpMe₂), 3.60-3.64 (m, 4H, α-THF), 7.23-7.30 (m, 6H, m-/ o-,p-Ph), 7.61–7.65 (m, 4H, o-/m-Ph) ppm. $^{13}\mathrm{C}$ NMR (100.6 MHz, C_6D_6) δ -1.2 (br s, CH₂Li), 10.8 (d, ${}^{3}J_{CP}$ = 1.3 Hz, 2,5-CpMe₂), 12.9 (s, 3,4-CpMe₂), 25.1 (s, β -THF), 68.8 (s, α -THF), 92.0 (d, ${}^{1}J_{CP} = 114.6$ Hz, 1-Cp), 115.5 (d, ${}^{2}J_{CP} = 12.2$ Hz, 2,5-Cp), 116.0 (d, ${}^{3}J_{CP} = 13.6$ Hz, 3,4-Cp), 128.2 (d, ${}^{3/2}J_{CP} = 10.9$ Hz, m-/o-Ph), 130.3 (d, ${}^{4}J_{CP} = 2.0$ Hz, p-Ph), 132.4 (d, ${}^{2/3}J_{CP} = 9.6$ Hz, o-/m-Ph), 136.2 (d, ${}^{1}J_{CP} = 2.0$ Hz, p-Ph), 132.4 (d, ${}^{2/3}J_{CP} = 9.6$ Hz, o-/m-Ph), 136.2 (d, ${}^{1}J_{CP} = 2.0$ Hz, p-Ph), 136.2 (d, ${}^{1}J_{CP} = 2.0$ Hz, 76.3 Hz, ipso-Ph) ppm. ¹³C NMR (100.6 MHz, THF-d₈) δ 0.7 (d, ¹J_{CP} = 41.2 Hz, PCH₂), 11.5 (d, ${}^{3}J_{CP}$ = 1.7 Hz, 2,5-CpMe₂), 14.0 (s, 3,4-Cp Me_2), 26.3 (s, β -THF), 68.2 (s, α -THF), 87.3 (d, ${}^{1}J_{CP} = 117.6$ Hz, 1-Cp), 115.5 (s, 2,5-/3,4-Cp), 115.7 (d, 3,4-/2,5-Cp), 128.1 (d, ^{3/2}J_{CP} = 10.5 Hz, m/o-Ph), 129.8 (d, ${}^{4}J_{CP}$ = 2.0 Hz, p-Ph), 133.1 (d, ${}^{2/3}J_{CP}$ = 9.5 Hz, o-/m-Ph), 140.2 (d, ${}^{1}J_{CP}$ = 74.0 Hz, ipso-Ph) ppm. ${}^{31}P$ NMR (162.0 MHz, pentane): δ 23.1 ppm. ³¹P NMR (162.0 MHz, C₆D₆): δ 22.3 ppm. ³¹P NMR (162.0 MHz, THF- d_8): δ 21.0 ppm. ⁷Li NMR (155.5 MHz, pentane): δ –5.20 ppm. ⁷Li NMR (155.5 MHz, C₆D₆): δ -5.54 ppm. ⁷Li NMR (155.5 MHz, THF- d_8): δ -0.89 ppm. IR: 3051 (w), 2951 (m), 2904 (m), 2853 (m), 1480 (s), 1304 (s), 1097 (s), 858 (s), 690 (s), 522 (s), 490 (s) cm^{-1}

 $\begin{array}{l} [(Li-CH_2-PMe_2-C_5Me_4)_2] \ (10). \ ^1\mathrm{H} \ \mathrm{NMR} \ (300.1 \ \mathrm{MHz}, \ \mathrm{C}_6\mathrm{D}_6): \ \delta \\ -0.46 \ (\mathrm{d}, \ ^2J_{\mathrm{HP}} = 11.7 \ \mathrm{Hz}, \ 2\mathrm{H}, \ \mathrm{PCH}_2\mathrm{Li}), \ 1.16 \ (\mathrm{d}, \ ^2J_{\mathrm{HP}} = 12.1 \ \mathrm{Hz}, \ 6\mathrm{H}, \\ \mathrm{PMe}_2), \ 2.20 \ (\mathrm{s}, \ 6\mathrm{H}, \ 3,4\text{-}\mathrm{CpMe}_2), \ 2.25 \ (\mathrm{s}, \ 6\mathrm{H}, \ 2,5\text{-}\mathrm{CpMe}_2) \ \mathrm{ppm}. \ ^1\mathrm{H} \\ \mathrm{NMR} \ (250 \ \mathrm{MHz}, \ \mathrm{THF}\text{-}d_8): \ \delta \ -0.56 \ (\mathrm{d}, \ ^2J_{\mathrm{HP}} = 7.5 \ \mathrm{Hz}, \ 2\mathrm{H}, \ \mathrm{PCH}_2), \\ 1.51 \ (\mathrm{d}, \ ^2J_{\mathrm{HP}} = 12.5 \ \mathrm{Hz}, \ 6\mathrm{H}, \ \mathrm{PMe}_2), \ 1.88 \ (\mathrm{s}, \ 6\mathrm{H}, \ 3,4\text{-}\mathrm{CpMe}_2), \ 2.13 \ (\mathrm{s}, \ 6\mathrm{H}, \ 2,5\text{-}\mathrm{CpMe}_2) \ \mathrm{ppm}. \ ^{13}\mathrm{C} \ \mathrm{NMR} \ (62.5 \ \mathrm{MHz}, \ \mathrm{THF}\text{-}d_8): \ \delta \ 4.75 \ (\mathrm{d}, \ ^1J_{\mathrm{CP}} \\ = 44.4 \ \mathrm{Hz}, \ \mathrm{PCH}_2), \ 11.39 \ (\mathrm{d}, \ ^4J_{\mathrm{CP}} = 1.88 \ \mathrm{Hz}, \ 2,5\text{-}\mathrm{CpMe}_2), \ 14.12 \ (\mathrm{s}, \ 3,4\text{-}\mathrm{PM}_2), \ 14.12 \ (\mathrm{s}, \ 3,4\text{-}\mathrm{P$

CpMe₂), 22.76 (d, ${}^{1}J_{CP} = 51.3$ Hz, PMe₂), 91.7 (d, ${}^{1}J_{CP} = 108.1$ Hz, 1-Cp), 113.7 (d, ${}^{3}J_{CP} = 13.1$ Hz, 3,4-Cp), 114.3 (d, ${}^{2}J_{CP} = 14.4$ Hz, 2,5-Cp) ppm. ${}^{31}P$ NMR (121.5 MHz, C₆D₆): δ 10.3 ppm. ${}^{31}P$ NMR (161.9 MHz, THF- d_8): δ 5.1 ppm. ${}^{7}Li$ NMR (155.4 MHz, pentane): δ -5.92 ppm. ${}^{7}Li$ NMR (155.4 MHz, C₆D₆): δ -6.36 ppm. ${}^{7}Li$ NMR (155.4 MHz, THF- d_8): δ 1.11 ppm. IR: 2910 (bs), 2858 (bs), 1387 (w), 1308 (s), 1018 (w), 938 (m), 899 (m), 765 (s), 692 (m), 464 (s) cm⁻¹.

 $[(Li-CH_2-PPh_2-C_5H_3tBu)_2]$ (11). ¹H NMR (500.1 MHz, C₆D₆): δ 0.05 (d, ${}^{2}J_{HP} = 9.0$ Hz, 2H, PCH₂Li), 1.45 (s, 9H, C₅H₃tBu), 6.28-6.32 (m, 2H, C₅H₃tBu), 6.44–6.43 (m, 1H, C₅H₃tBu), 7.20–6.94 (m, 6H, o-/m,p-Ph), 7.61-7.30 (m, 4H, m-/o-Ph) ppm. ¹H NMR (400.1 MHz, THF- d_8): δ -0.01 (d, ${}^{2}J_{HP}$ = 12.0 Hz, 2H, PCH₂), 1.19 (s, 9H, C₅H₃tBu), 5.76-5.91 (m, 3H, C₅H₃tBu), 7.24-7.66 (m, 10H, PPh₂) ppm. ¹³C NMR (100.6 MHz, C_6D_6): δ –4.9 (br s, PCH₂), 32.0 (s, $C(CH_3)_3$, 33.1 (s, $C(CH_3)_3$), 96.7 (d, ${}^{1}J_{CP} = 115.8$ Hz, $1-C_5H_3tBu$), 106.8 (br s, 2-C₅H₃tBu), 111.0 (d, ${}^{3}J_{CP} = 16.7$ Hz, 4-C₅H₃tBu), 111.0 $(d, {}^{2}J_{CP} = 9.8 \text{ Hz}, 5 \cdot C_{5}H_{3}tBu), 130.4 (br s, o-Ph), 131.7 (d, {}^{3}J_{CP} = 9.5$ Hz, m-Ph), 135.8 (s, p-Ph), 136.0 (d, ${}^{1}J_{CP} = 94.2$ Hz, ipso-Ph), 138.8 $(d, {}^{3}J_{CP} = 14.4 \text{ Hz}, 3-C_{5}H_{3}tBu)$ ppm. ${}^{13}C$ NMR (62.5 MHz, THF- d_{8}): δ -2.7 (d, ${}^{1}J_{CP}$ = 38.8 Hz, PCH₂), 32.6 (s, C(CH₃)₃), 33.7 (s, $C(CH_3)_3$, 75.4 (d, ${}^{1}J_{CP}$ = 125.5 Hz, 1- C_5H_3tBu), 107.8 (d, ${}^{2}J_{CP}$ = 15.6 Hz, 2-C₅H₃tBu), 112.6 (d, ${}^{3}J_{CP}$ = 18.1 Hz, 4-C₅H₃tBu), 115.4 (d, ${}^{2}J_{CP}$ = 15.6 Hz, 5- C_5H_3tBu), 127.7 (d, ${}^2J_{CP}$ = 10.6 Hz, o-Ph), 130.4 (d, ${}^1J_{CP}$ = 85.6 Hz, *ipso*-Ph), 132.5 (d, ${}^{3}J_{CP}$ = 9.4 Hz, *m*-Ph), 132.6 (d, ${}^{4}J_{CP}$ = 2.5 Hz, p-Ph), 140.7 (s, $3-C_5H_3tBu$) ppm. ³¹P NMR (121.5 MHz, hexane): δ 21.4 ppm. ³¹P NMR (161.9 MHz, THF- d_8): δ 20.3 ppm. ^{31}P NMR (161.9 MHz, C₆D₆): δ 23.1 ppm. ^7Li NMR (155.4 MHz, pentane): δ – 5.98 ppm. ⁷Li NMR (155.4 MHz, C₆D₆): δ – 5.89 ppm. ⁷Li NMR (155.4 MHz, THF-d₈): δ 0.92 ppm. IR: 2953 (w), 2858 (w), 1435 (m), 1200 (m), 1174 (w), 1088 (m), 1054 (m), 1026 (m), 713 (s), 691 (s), 531 (s) cm⁻¹

 $[(Li-CH_2-PMe_2-C_5H_3tBu)_2]$ (12). ¹H NMR (300.1 MHz, C₆D₆): δ -0.59 (d, ${}^{2}J_{HP} = 12.3$ Hz, 2H, PCH₂), 1.06 (d, ${}^{2}J_{HP} = 12.5$ Hz, 6H, PMe₂), 1.42 (m, 4H, β-THF), 1.50 (s, 9H, C₅H₃tBu), 3.57 (m, 4H, α-THF), 6.15 (m, 1H, 4-C₅H₃tBu), 6.18 (m, 1H, 2-C₅H₃tBu), 6.32 (m, 1H, 5-C₅H₃tBu) ppm. ¹H NMR (250.0 MHz, THF- d_8): δ –0.59 (d, ${}^{2}J_{\text{HP}}$ = 10.0 Hz, 2H, PCH₂Li), 1.20 (s, 9H, C₅H₃tBu), 1.42 (d, ${}^{2}J_{\text{HP}}$ = 12.5 Hz, 6H, PMe2), 5.70-5.65 (m, 1H, 4-C5H3tBu), 5.70-5.72 (m, 1H, 2-C₅H₃tBu), 5.82–5.77 (m, 1H, 5-C₅H₃tBu) ppm. ¹³C NMR (75.5 MHz, C₆D₆): δ -4.2 (br s, PCH₂Li), 19.7 (d, ¹J_{CP} = 48.6 Hz, PMe), 19.9 (d, ${}^{1}J_{CP}$ = 47.9 Hz, PMe), 25.8 (s, β -THF), 32.2 (s, $C(CH_3)_3)$, 33.4 (s, $C(CH_3)_3)$, 67.8 (s, α -THF), 82.0 (br s, 1- C_5H_3tBu), 103.6 (d, ${}^3J_{CP} = 13.9$ Hz, 4- C_5H_3tBu), 106.0 (d, ${}^2J_{CP} = 11.6$ Hz, 5-C₅H₃tBu), 107.9 (d, ${}^{2}J_{CP}$ = 14.4 Hz, 2-C₅H₃tBu), 138.1 (d, ${}^{3}J_{CP}$ = 13.9 Hz, 3-C₅H₃tBu) ppm. 13 C NMR (62.5 MHz, THF-d₈): δ -0.13 (d, ${}^{1}J_{CP} = 39.4$ Hz, PCH_{2}), 21.2 (d, ${}^{1}J_{CP} = 52.5$ Hz, PMe_{2}), 32.4 (s, $C(CH_{3})_{3}$), 33.5 (s, $C(CH_{3})_{3}$), 97.1 (d, ${}^{1}J_{CP} = 112.5$ Hz, $1-C_{5}H_{3}tBu$), 104.8 (d, ${}^{2}J_{CP}$ = 14.4 Hz, 2-/5-C₅H₃tBu), 106.7 (d, ${}^{2}J_{CP}$ = 14.4 Hz, 2-/ $5-C_{\rm S}H_{\rm 3}tBu$), 109.1 (d, ${}^{3}J_{\rm CP}$ = 13.1 Hz, $4-C_{\rm S}H_{\rm 3}tBu$), 135.9 (d, ${}^{3}J_{\rm CP}$ = 13.8 Hz, 3-C₅H₃tBu) ppm. ³¹P NMR (161.9 MHz, C₆D₆): δ 7.0 ppm. ^{31}P NMR (161.9 MHz, THF- d_8): δ 6.25 ppm. ^7Li NMR (155.4 MHz, THF- d_8): δ -2.39 ppm. IR: 2964 (s), 2941 (s), 1198 (m), 1091 (m), 943 (s), 899 (m), 797 (s), 737 (s), 713 (s), 687 (s), 493 (m), 433 (m) cm⁻

[(Cu-CH₂-PPh₂-C₅Me₄)₂] (13). 9 was prepared in situ according to route B (theoretical yield: 1.40 mmol), dissolved in toluene (10 mL), and cooled to -78 °C. A suspension of CuCl (139 mg, 1.40 mmol) in toluene (8 mL) was cooled to -78 °C and added slowly. The reaction mixture was warmed to ambient temperature over a period of 12 h. After another 28 h, the suspension was filtered and the residue washed with toluene (2 × 8 mL). All volatiles were removed from the filtrate to give a colorless solid that was washed with pentane (4 × 20 mL) and dried in vacuo. Yield (over 2 steps): 333 mg, 416 μ mol, 59%.

¹H NMR (300.1 MHz, C_6D_6): δ 1.46 (d, 2H, ² J_{HP} = 13.9 Hz, *CH*₂), 1.97 (s, 6H, 2,5-Cp*Me*₂), 2.18 (s, 6H, 3,4-Cp*Me*₂), 6.98-7.03 (m, 6H, *o*-*p*-Ph), 7.68-7.74 (m, 4H, *m*-Ph) ppm. ¹³C NMR (100.6 MHz, C_6D_6): δ 6.0 (d, ¹ J_{CP} = 37.7 Hz, *CH*₂), 11.5 (s, 3,4-Cp*Me*₂), 13.6 (s, 2,5-Cp*Me*₂), 86.5 (d, ¹ J_{CP} = 113.0 Hz, 1-Cp), 117.0 (d, ^{2/3} J_{CP} = 12.1 Hz, 3,4/2,5-Cp), 118.1 (d, ${}^{3/2}J_{CP}$ = 14.3 Hz, 2,5-/3,4-Cp), 128.5 (d, ${}^{2}J_{CP}$ = 11.3 Hz, o-Ph), 130.9 (d, ${}^{4}J_{CP}$ = 1.3 Hz, p-Ph), 133.2 (d, ${}^{3}J_{CP}$ = 9.8 Hz, m-Ph), 134.8 (d, ${}^{1}J_{CP}$ = 77.6 Hz, *ipso*-Ph) ppm. ${}^{31}P$ NMR (121.5 MHz, C₆D₆): δ 20.4 ppm. ${}^{31}P$ NMR (121.5 MHz, Tol): δ 21.2 ppm. IR: 3053 (w), 2906 (m), 2856 (s) 1435 (s), 1299 (s), 1103, (s), 900 (s), 810 (s), 803 (s), 746 (s), 692 (s), 585 (s), 481 (s) cm⁻¹.

X-ray Crystallographic Studies. Crystal data were collected with a Stoe-IPDSII area-detector diffractometer using graphite-monochromated Mo K α radiation (λ = 71.073 pm) at 100 K. The detector was placed at a distance of 1.2 cm from the crystal. Data reduction was carried out by using the IPDS software X-Area (Stoe).²⁹ The data were empirically corrected for absorption and other effects by using multiscans.³⁰ The structures were solved by direct methods (Sir-97)³¹ and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).³² The programs PLATON³³ and PLUTON³⁴ were used to check the results of the X-ray analyses.

ASSOCIATED CONTENT

S Supporting Information

Experimental details for compounds 1–4, CIF files giving crystallographic data for compounds 5a,b, 6, 9, and 11, figures giving ¹H, ³¹P, ⁷Li and ¹³C NMR spectra of the complexes, and text giving additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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