EurJIC European Journal of Inorganic Chemistry

FULL PAPER

DOI: 10.1002/ejic.201200407

Bis-Ylide Ligands from Acyclic Proximal Diphosphonium Precursors

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Keywords: Ylides / Ylide ligands / Phosphorus / Rhodium / Electrostatic interactions

1,2- or 1,3-Phenylene-diphosphonium bis-ylides have been prepared and their stabilities compared by analysis of the effects of the substitution pattern of the phenylene bridge and the steric hindrance of the *P*-alkyl substituents in the diphosphonium precursors $RPh_2P^+(C_6H_4)^+PPh_2R'$ (R,R′ = Me, Et). In the *o*-phenylene series, the vicinity of the phosphorus centers allows the distal P^+/C^- charge separation of the mono-ylide intermediate to be canceled by the formation of a cyclic ylidophosphorane. The ring strain in the latter was released through phenylene–P(σ^5) bond cleavage to afford relaxed diphosphonium bis-ylides, which were isolated as carbodiphosphorane, or protonated in situ to form bis-phosphonium ylides depending on the bulkiness of the *P*-alkyl substituents. In the *m*-phenylene series (with R,R′ = Me), the amplified distal P^+/C^- charge separation proved sufficient to stabilize the corresponding diphosphonium bis-ylide as a chelating ligand of an $Rh^I(CO)_2$ center, in a complex where the effective σ-donation of the ligand was confirmed by comparison of the IR carbonyl stretching frequencies with those of the isostructural complex previously described in the *o*-phenylene series.

Introduction

Beyond their ubiquitous role in organic synthesis as Wittig-type reactants for the olefination of carbonyl compounds, phosphonium ylides in their more or less stabilized versions exhibit rich coordination chemistry as carbon ligands of transition metals[1] in either a mono- or bidentate manner. In general, chelating ligands have been designed to control not only the electron-donating properties, but also the stability and stereoselectivity of complexation.[2]

A general classification of diphosphonium bis-ylides has recently been proposed based on the bridge length (from fused to ω- and α-bis-ylides) and the orientation of the P^+–C^-/P^+–C^- sequence (head-to-head, tail-to-tail, or head-to-tail).[3] The preparation and stability of cyclic head-to-head diphosphonium bis-ylides constrained in five-, six-, and seven-membered rings have been systematically compared.[4] Indeed, although the fused bis-ylide **2** and the β-bis-ylide **4** are stable, the α-bis-ylide **3a** is destabilized by the repulsion between the two vicinal negative charges, leading, after fragmentation, to *o*-bis(diphenylphosphanyl)-benzene (*o*-ddpb, **1**) and acetylene. Nevertheless, delocalization of the negative charge over the carbonyl C-substituents allowed the α-bis-ylide **3b** to be isolated (Scheme 1).[3] It thus appears that only the cyclic diphosphonium bis-ylides **2** and **4** can be used as ligands for electron-rich complexes.

The acyclic analogues of these bis-ylides, in which the covalent constraint is minimized, have been investigated in detail, with both *o*- and *m*-phenylene bridges. The results are disclosed herein and discussed by comparison to their cyclic analogues.[3]

Results and Discussion

Previously Obtained Preliminary Results: Dimethyl *o*-Phenylene-Diphosphonium 5

The acyclic dimethyl diphosphonium **5** was readily prepared in 90% yield by reaction of *o*-dppb[5] (**1**) with an excess of methyl triflate (Figure 1).[4] All attempts at generating the corresponding bis-ylide **6** by deprotonation were, however, unsuccessful. This was attributed to the formation of the cyclic five-membered-ring ylide **7**, which results from instant attack of the mono-ylide intermediate at the adjacent phosphonium center. The cyclic ylidophosphorane **7**, which exists as a mixture of two stereoisomers in a 95:5 ratio corresponding to different occupations of the axial and equatorial positions of the trigonal-bipyramidal configuration, was shown to slowly rearrange into the carbodiphosphorane **8** upon phenylene–P(σ^5) bond cleavage (Scheme 2),[6] in accord with the mechanism for the transformation **5**→**8**, reported previously by Schmidbaur et al.[7]

In view of the unfavorable formation of ylidophosphoranes of type **7**, more hindered ethyl substituents were intro-

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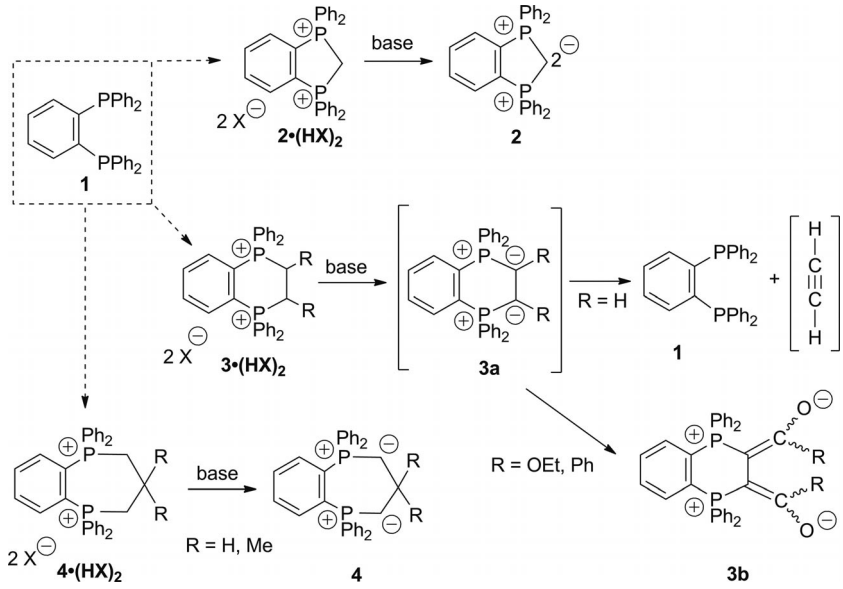
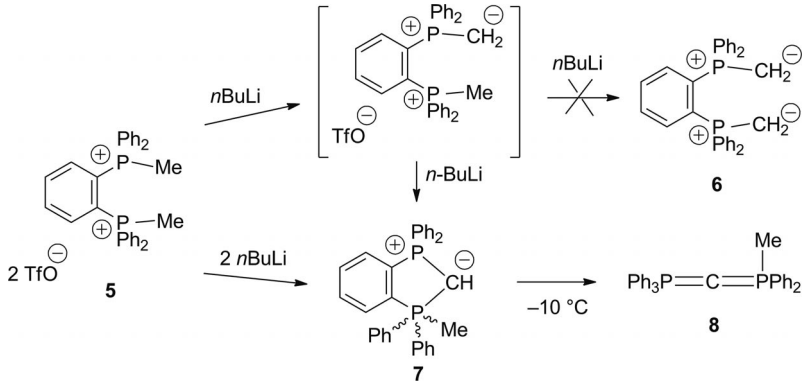


Scheme 1. Vicinal *o*-phenylene-bridged diphosphoniums **2**–**4**·**(HX)$_2$** salts and ylides thereof.



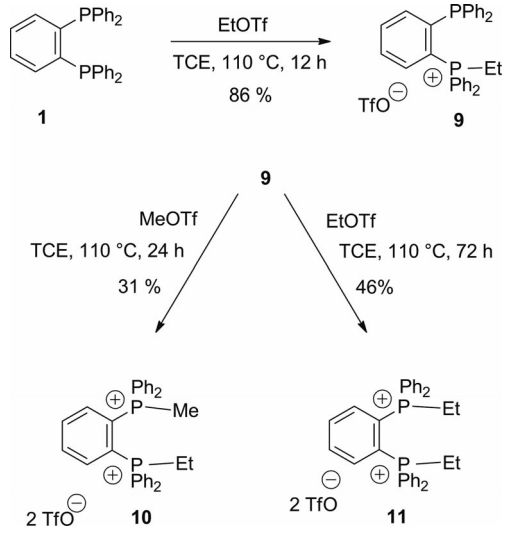
Scheme 2. Preparation of the carbodiphosphorane **8** from the acyclic diphosphonium **5** via the cyclic ylidophosphorane **7**.

duced at the phosphorus atoms through the preparation of the mixed ethyl methyl diphosphonium **10** and the diethyl homologue **11**.

P-Ethyl-Substituted *o*-Phenylene-Diphosphoniums 10 and 11

The diphosphane **1** was treated with ethyl triflate in 1,1,2,2-tetrachloroethane (tce) at 110 °C for 12 h to give the phosphanyl-phosphonium cation **9** in 86% yield.[8] A second alkylation reaction with methyl triflate in the same solvent at 110 °C for 24 h allowed the mixed diphosphonium **10** to be isolated in 31% yield (Scheme 3). The more sterically demanding diethyl diphosphonium **11** was then obtained in 46% yield by treatment of the phosphonium **9** with an excess of ethyl triflate (7 equiv.) in tce for 72 h (Scheme 3).

The ^{31}P NMR chemical shifts observed for **10** and **11** are characteristic of phosphonium derivatives [**10**: δ_P = +26.3 ppm, d, J_{PP} = 6.1 Hz, and +29.7 ppm, d, J_{PP} = 6.1 Hz; **11**: δ_P = +30.6 ppm, s]. Their structures were unam-



Scheme 3. Preparation of the acyclic diphosphoniums **10** and **11** from *o*-dppb via the mono-ethyl phosphonium **9**.

biguously confirmed by X-ray diffraction analysis of colorless single crystals (Figure 1).[9] The steric strain is revealed by the torsional P1–C1–C2–P2 bond angles at the *o*-phenylene bridge, which increase significantly from the less-hindered dimethyl diphosphonium **5** to the more hindered diethyl diphosphonium **11** (**5**: 2.5°; **10**: 6.4°; **11**: 13.4°). These values can be attributed to both electrostatic and steric repulsions between the phosphonium fragments. The introduction of a second ethyl substituent also results in an increase in the *trans* annular $P^+\cdots P^+$ distance (3.73 Å in **11** vs. 3.66 Å in **10**), enforced by the steric strain and still induced by the electrostatic repulsion.

The bis-ylide **10b** was first envisaged by deprotonation of **10** with 2 equiv. of *n*-butyllithium in thf at –78 °C. Multinuclear NMR monitoring showed the immediate disappearance of the starting diphosphonium **10** with concomitant formation of the five-membered cyclic ylide **10c** as a mixture of two stereoisomers in a ratio of 95:5. As in the case of the dimethyl analogue, the ylidophosphorane **10c** results from nucleophilic attack of the mono-ylide at the vicinal phosphonium center of the first mono-ylide intermediate **10a**. The initial deprotonation step occurred at the most acidic alkyl substituent, namely the $P^+–CH_3$ moiety (Scheme 4).

The structure of **10c** was first assigned on the basis of the ^{31}P NMR analysis (δ_P = –1.6 and –89.8 ppm; J_{PP} = 57.6 Hz for the major isomer). The CH ylide moiety was evidenced by ^1H and ^{13}C NMR spectroscopy [δ_{CH} = +0.43 ppm, dd, $J_{HP(\sigma4)}$ = 20.0, $J_{HP(\sigma5)}$ = 15.0 Hz; δ_{CH} = +13.1 ppm, dd, $J_{CP(\sigma4)}$ = 113.0, $J_{CP(\sigma5)}$ = 167.0 Hz]. As in the case of **7** (see Scheme 2), the existence of two stereoisomers is explained by the trigonal-bipyramidal geometry at the pentacoordinate phosphorus center. Finally, the cyclic intermediate **10c** underwent protonative rearrangement to the open bis-phosphonium ylide **10e**, which was isolated in 62% overall yield.[10] The latter appeared as an AX system in the ^{31}P NMR spectrum [δ_P = +19.3 ppm, d, J_{PP} = 24.3 Hz (PPh_3); +24.2 ppm, d, J_{PP} = 24.3 Hz (PPh_2Et)]. The ylidic CH fragment was also evidenced by ^1H and ^{13}C NMR spectroscopy (δ_{CH} = +2.05 ppm, pseudo-t, J_{HPPh3} = $J_{HPPh2Et}$ = 5.0 Hz; δ_{CH} = –6.3 ppm, dd, J_{CPPh3} = 122.0, J_{CPh2Et} = 124.6 Hz). The formation of **10e** results from the protonation of the diphosphonium bis-ylide intermediate **10d**, which was characterized at –30 °C by ^{31}P and ^{13}C NMR spectroscopy [δ_P = +40.2 ppm, d, ($Ph_2P^+C_2$); +31.9 ppm, d, (Ph_3P^+C), J_{PP} = 51.6 Hz; δ_{CH} = +5.6 ppm, br. s, and +13.7 ppm, m]. The latter was generated by phenylene–P(σ^5) bond cleavage via the putative transient phenylide phosphonium intermediate **I** (Scheme 4).

As a single ethyl substituent was not sufficient to prevent intramolecular rearrangement to the cyclic ylidophosphorane **10c**, the deprotonation reaction was tested starting from the more hindered diethyl diphosphonium **11**. Again, the addition of 2 equiv. of *n*-butyllithium in [D_8]thf at –78 °C was monitored by multinuclear NMR methods. In spite of the presence of the bulkier ethyl substituents at both the P atoms, the cyclic ylidophosphorane **11c** was again formed, as indicated by the corresponding ^{31}P chemi-

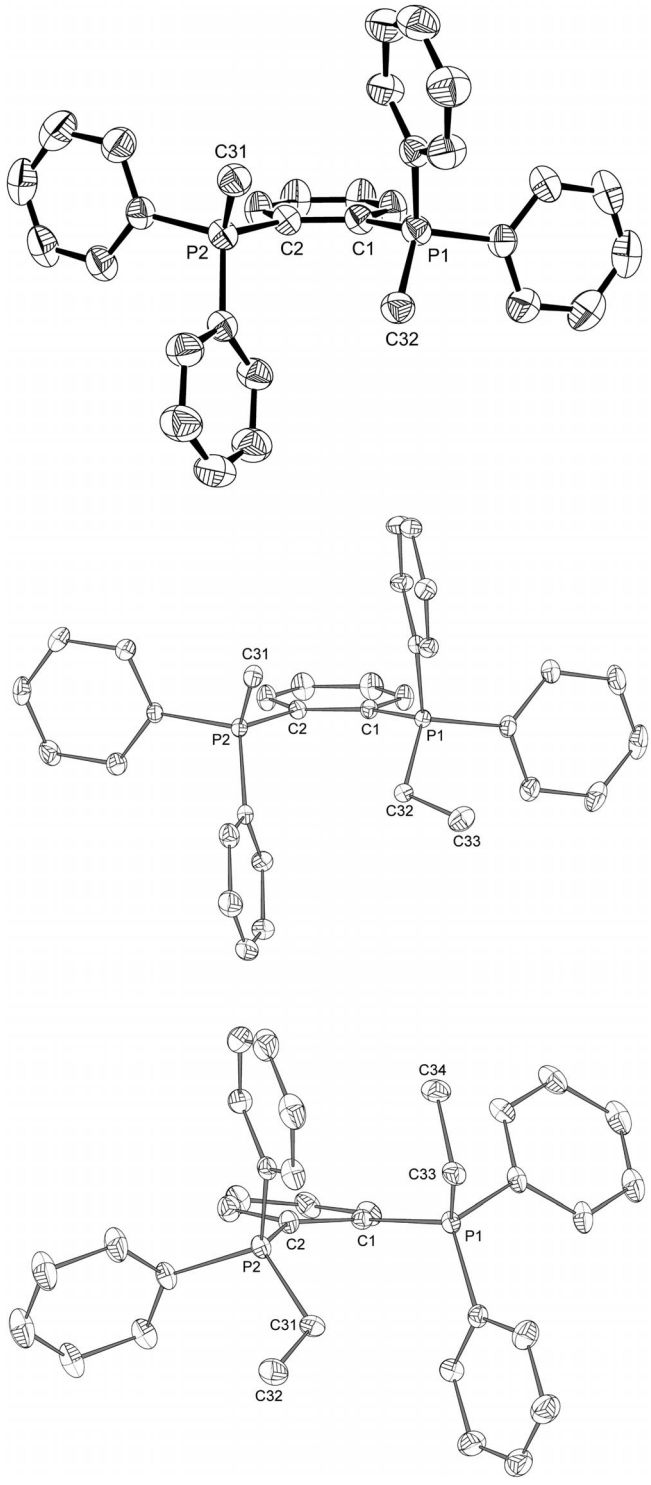
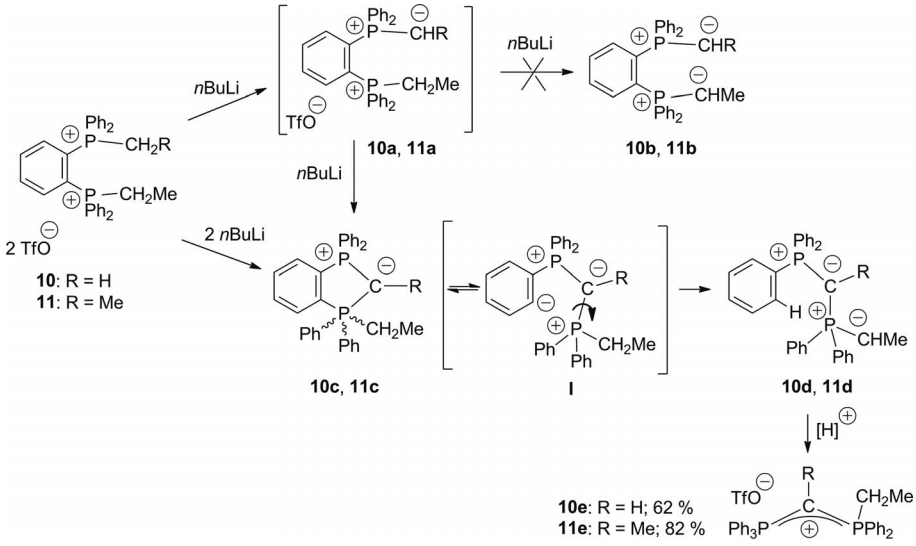


Figure 1. Views of the X-ray crystal structures of the diphosphoniums **5** (top), **10** (middle), and **11** (bottom), with thermal ellipsoids drawn at the 30% probability level (the triflate anions and H atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°] for **5**: C1–P1 1.823(4), C32–P1 1.778(4), C1–C2 1.429(8), P1–C1–C2 128.56(12), C1–P1–C32 113.71(18);[4] for **10**: C1–P1 1.8279(17), C2–P2 1.8206(17), C32–P1 1.8058(18), C1–C2 1.428(2), P1–C1–C2 127.94(12), P2–C2–C1 127.54(13), C1–P1–C32 112.63(8); for **11**: C1–P1 1.826(3), C2–P2 1.817(3), C33–P1 1.800(3), C1–C2 1.428(4), P1–C1–C2 129.3(2), P2–C2–C1 128.4(2), C1–P1–C33 114.79(14).



Scheme 4. Preparation of the bis-phosphonium ylides **10e** and **11e** from the acyclic diphosphoniums **10** and **11** via the cyclic ylidophosphoranes **10c** and **11c** and the diphosphonium bis-ylides **10d** and **11d**, respectively.

cal shifts (δ_P = +10.1, –88.3 ppm; J_{PP} = 94.2 Hz). The presence of an ylidic *C*-Me moiety was confirmed by ^{13}C NMR spectroscopy [δ_{CMe} = +5.7 ppm, dd, $J_{CP(\sigma4)}$ = 120.0, $J_{CP(\sigma5)}$ = 172.0 Hz; δ_{CCH3} = +12.6 ppm, pseudo-t, $J_{CP(\sigma4)}$ = $J_{CP(\sigma5)}$ = 13.8 Hz]. In contrast to the previous cases, a single stereoisomer of **11c** was observed, likely because of the enhanced hindrance of the ethyl substituent. By variable-temperature ^{31}P NMR monitoring up to room temperature, the cyclic intermediate **11c** was shown to undergo protonative rearrangement to the bis-phosphonium ylide **11e** [δ_P = +25.4 ppm, d, J_{PP} = 53.7 Hz (PPh_3); +28.8 ppm, d, J_{PP} = 53.7 Hz (PPh_2Et)] in 82% overall yield, likely by a mechanism similar to that proposed for the **10c**→ **10e** transformation (Scheme 4). The structure of **11e** was assigned on the basis of the ^1H and ^{13}C NMR spectra (δ_{CCH3} = +1.83 ppm, pseudo-t, J_{HPPh3} = $J_{HPPh2Et}$ = 15.0 Hz; δ_{CMe} = –2.0 ppm, br. s). The exact structure of **11e** was obtained by X-ray diffraction analysis of a single crystal deposited from CH_2Cl_2 (Figure 2).[9] The cation exhibits a delocalized diphosphorallyl structure with a central sp^2-hybridized planar tricoordinate ylidic carbon center (Σ°-C1 = 359.68°) and similar P–C(sp^2) bond lengths [C1–P1 1.7230(14), C1–P2 1.7135(14) Å], revealing a resonance structure between canonical C–P (ca. 1.80–1.85 Å) and C=P (ca. 1.60–1.65 Å) bond types.[11] The system features a distorted U-shaped H_5C_6–Ph_2P–C(Me)–PPh_2–CH_2Me four-bond sequence.

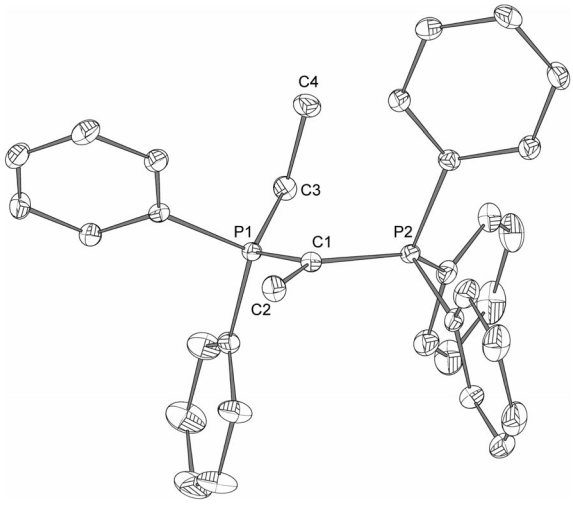
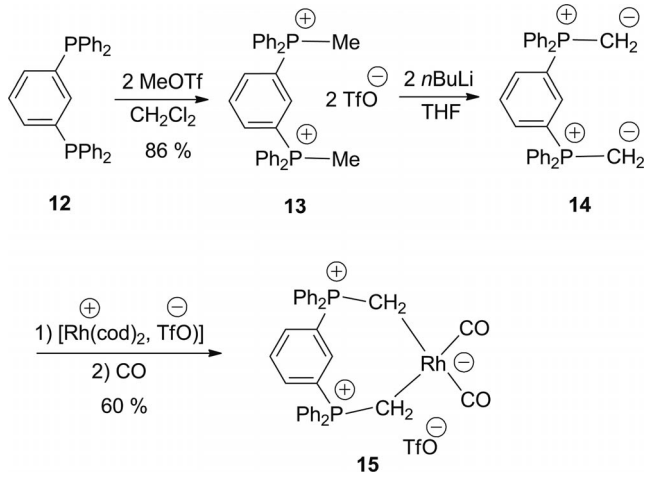


Figure 2. View of the X-ray crystal structure of the bis-ylide **11e** with thermal ellipsoids drawn at the 30% probability level (the triflate anions and H atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°].C1–P1 1.7230(14), C1–P2 1.7135(14), C3–P1 1.8223(15), C1–C2 1.529(2), P1–C1–P2 123.89(8), P1–C1–C2 118.11(10), C1–P1–C3 117.84(7).

The *m*-phenylene bridge then was envisaged as an alternative for separating the two phosphonium fragments in remote positions.

Dimethylated *m*-Phenylene-Diphosphonium 13

1,3-Bis(diphenylphosphanyl)benzene (**12**) was first prepared by following a recent procedure reported by James and co-workers.[12] The addition of 2 equiv. of methyl triflate to **12** in CH_2Cl_2 afforded the targeted *m*-phenylene-diphosphonium **13** in 86% yield (Scheme 5). The single ^{31}P NMR signal (δ_P = +22.5 ppm, s) is in agreement with a symmetrical structure in solution. The static structure was determined by X-ray diffraction analysis of single crystals deposited from a CH_2Cl_2/pentane mixture at –20 °C (Figure 3).[9] In contrast to the *ortho*-disubstituted diphosphoniums **5**, **10**, and **11**, the bond angles at the sp^2 carbon atoms of the *m*-phenylene bridge in **13** are very close to the ideal VSEPR values (deviation of ca. 0.9° only). As expected, the $P^+\cdots P^+$ distance (ca. 5.55 Å) is longer than the corresponding sum of the van der Waals radii (3.80 Å), thus confirming the absence of steric/electrostatic strain between the phosphonium centers. This could a priori favor the formation of a more stable bis-ylide.



Scheme 5. Synthesis of the bis-ylide dicarbonylrhodium complex **15** from *m*-dppb (**12**).

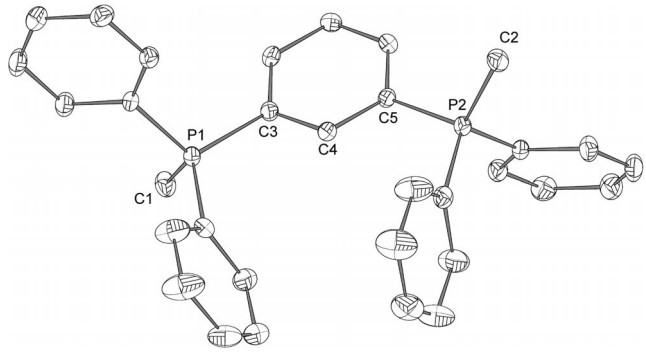


Figure 3. View of the X-ray crystal structure of the diphosphonium **13** with thermal ellipsoids drawn at the 30% probability level (the triflate anions and H atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–P1 1.785(3), C2–P2 1.780(3), C3–P1 1.804(2), C5–P2 1.796(2), C2–P2–C5 110.04(13), C1–P1–C3 108.62(12), P2–C5–C4 120.25(18), P1–C3–C4 121.48(17).

Deprotonation of the *m*-phenylene-diphosphonium **13** was then investigated by anticipating that the distance between the two phosphonium fragments would be sufficient to prevent the rearrangement. And indeed, NMR monitoring of the deprotonation of **13** with 2 equiv. of *n*-BuLi in [D_8]thf at low temperature allowed the expected acyclic bis-ylide **14** to be identified. This result confirms the greater acidity of the sp^3 CH_3 groups at the phosphonium fragments with respect to the central sp^2 CH group of the *m*-phenylene bridge. The ^{31}P NMR spectrum of the solution displays a single signal at +19.6 ppm, which gives a first indication of the nature and symmetry of the environment of the phosphorus atoms. The structure of **14** was confirmed by ^1H and ^{13}C NMR spectroscopy, in particular, by high-field signals assigned to the methylene groups at δ_H = +0.1 ppm (d, J_{HP} = 7.5 Hz) and δ_C = –5.9 ppm (d, J_{CP} = 98.1 Hz). Note, by warming the [D_8]thf solution to room temperature, slow decomposition of the bis-ylide **14** was observed, resulting in a mixture of unidentified products.

The coordination behavior of **14** with a Rh^I fragment was investigated by performing both the complexation and the cod/$(CO)_2$ exchange steps in situ in a one-pot sequence. The addition of a stoichiometric amount of [$Rh(cod)_2$][TfO] to a thf solution of the bis-ylide **14** followed by treatment with an excess of CO thus led to the targeted rhodium-(dicarbonyl) bis-ylide complex **15** in 60% overall yield (from **13**). The presence of a single signal in the ^{31}P NMR spectrum (δ_P = +35.6 ppm) indicates a symmetrical structure in solution. The significant shift of the ^{31}P signal with respect to the free bis-ylide is in agreement with the expected ylide–rhodium complex structure. The Rh–CH_2 bond was evidenced by multinuclear NMR techniques and, in particular, by the high-field region and the multiplicity of the ^{13}C NMR signal of the metalated ylidic carbon atom (δ_{CH2} = +1.2 ppm, dd, J_{CP} = 40.3, J_{CRh} = 21.5 Hz). The symmetry of **15** was also demonstrated by the presence of a single ^{13}CO resonance at +186.3 ppm (d, J_{CRh} = 20.3 Hz) and the structure was finally confirmed by ESI-MS (*m*/*z* = 633.1 $[M]^+$). The carbonyl IR stretching absorptions, which are currently used for estimating the donor character of co-ligands, were found at low frequencies (ν_{CO} = 1983, 2053 cm^{-1} in CH_2Cl_2), very close to those reported for the analogous *ortho*-disubstituted rhodium complex (ν_{CO} = 1984, 2051 cm^{-1}).[6] These values confirm that the diphosphonium bis-ylide **14** can be considered a strongly donating carbon ligand and that the nature of the phenylene bridge (*ortho* vs. *meta* isomers) has no influence on the corresponding electronic properties.[13] Only the high-field value of the ^{103}Rh NMR chemical shift for **15** (δ = +477 ppm) with respect to the *ortho*-disubstituted species (δ = +983 ppm)[6] could be due to the cone shielding effect of the phenylene bridge, which is more sterically constrained above the Rh atom in **15** than in the *ortho* isomer.

However, the bis-ylide rhodium complex **15** proved unstable, decomposing in air or under an inert atmosphere to give a black precipitate. This chemical behavior might be explained by the zwitterionic rhodate structure involving two two-bond charge separations with a formal negative charge at the electropositive Rh^I center.[14] Complex **15** is the second reported example of a rhodate bis-ylide complex.[6]

Conclusion

The preparation and characterization of acyclic diphosphonium bis-ylides from the corresponding diphosphonium precursors have been systematically investigated with respect to the steric demand at the phosphorus centers and the substitution pattern of the phenylene bridge. In the *o*-phenylene series, more or less hindered bis-ylides (with H or Me C-substituents) were not observed due to the instability of the mono-ylide intermediates, which instantly rearrange to cyclic ylidophosphoranes (although bulkier Me C-substituents could be envisaged, like *i*Pr or *t*Bu, the enhanced nucleophilic character of the ylidic C atom could still exceed the anticipated steric stabilization of the mono-ylide). Subsequent cleavage of the phenylene–P(σ^5) bond of the ylidophosphorane allowed steric relaxation to bis-phos-

phonium ylides. In contrast, in the *m*-phenylene series, in which the two phosphonium centers are in remote positions, the bis-ylide could be fully characterized. By reaction with a cationic rhodium(I) precursor, the latter bis-ylide was shown to act as a strongly donating carbon ligand, generalizing recent observations in the *ortho* series.[6] The role of steric and electrostatic interactions in the control of structural and reactivity features of acyclic proximal diphosphoniums has been highlighted herein.

Experimental Section

General: Diethyl ether, toluene, and thf were dried and distilled from sodium/benzophenone, pentane, dichloromethane, 1,1,2,2-tetrachloroethane (tce), and acetonitrile over P_2O_5. All other reagents were used as commercially available. All reactions were carried out under argon using Schlenk and vacuum-line techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker DPX 300 and Avance 500 spectrometers. Chemical shifts (δ) are given in ppm with positive values to high frequency measured relative to tetramethylsilane for ^1H and ^{13}C NMR, and to H_3PO_4 for ^{31}P NMR. Coupling constants (J) are given in Hz. ^{103}Rh chemical shifts are given to high frequency from $\delta(^{103}Rh) = 3.16$ MHz.

Phosphonium 9: Ethyl trifluoromethanesulfonate (574 μL, 4.48 mmol) was added to a solution of **1** (2.0 g, 4.48 mmol) in tce (12.0 mL) and the solution was then stirred for 12 h at 110 °C. After evaporation of the solvent, the solid residue was washed with Et_2O (30.0 mL), affording **9** as a white powder (2.41 g, 86%); m.p. 68–69 °C. ^1H NMR (CD_3CN, 25 °C): δ = 7.85–7.50 (m, 14 H, H_{ar}), 7.42–7.22 (m, 6 H, H_{ar}), 6.99–6.90 (pseudo-t, $J_{HH} = J_{HP+}$ = 6.9 Hz, 4 H, H_{ar}), 3.57 (dq, J_{HH} = 7.5, J_{HP+} = 12.9 Hz, 2 H, CH_2), 1.37 (dt, J_{HH} = 7.5, J_{HP+} = 20.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_3CN, 25 °C): δ = 142.8 (dd, J_{CP+} = 14.9, J_{CP} = 14.9 Hz, C), 139.2 (d, J_{CP+} = 11.3 Hz, CH_{ar}), 136.5 (pseudo-t, $J_{CP+} = J_{CP}$ = 11.8 Hz, C), 135.1 (d, J_{CP+} = 2.8 Hz, CH_{ar}), 134.5 (d, J_{CP+} = 2.9 Hz, CH_{ar}), 133.3 (dd, J_{CP+} = 9.6, J_{CP} = 1.9 Hz, CH_{ar}), 133.0 (d, J_{CP} = 19.1 Hz, CH_{ar}), 131.6 (d, J_{CP} = 9.9 Hz, CH_{ar}), 131.3 (d, J_{CP+} = 12.4 Hz, CH_{ar}), 130.1 (d, J_{CP+} = 12.6 Hz, CH_{ar}), 129.5 (CH_{ar}), 128.8 (d, J_{CP} = 7.2 Hz, CH_{ar}), 125.3 (dd, J_{CP+} = 87.1, J_{CP} = 35.6 Hz, C), 120.7 (q, J_{CF} = 320.0 Hz, CF_3SO_3), 119.6 (dd, J_{CP+} = 86.3, J_{CP} = 2.6 Hz, C), 19.1 (dd, J_{CP+} = 53.2, J_{CP} = 15.0 Hz, CH_2), 7.3 (dd, J_{CP+} = 5.1, J_{CP} = 1.1 Hz, CH_3) ppm. ^{31}P NMR (CD_3CN, 25 °C): δ = +26.66 (d, J_{PP} = 23.1 Hz, P^+), –15.28 (d, J_{PP} = 23.1 Hz, P) ppm. MS (ES+): *m/z* = 475.2 $[M]^+$. HRMS (ES+): calcd. for $C_{32}H_{29}P_2$ $[M]^+$ 475.1744; found 475.1740.

Diphosphonium 10: Methyl trifluoromethanesulfonate (246 μL, 2.24 mmol) was added to a solution of **9** (0.70 g, 1.12 mmol) in tce (12.0 mL) and the solution was then stirred for 24 h at 110 °C. After evaporation of the solvent, an oily residue was isolated. Successive washing with toluene (2 × 30 mL), and Et_2O (2 × 30 mL) followed by recrystallization at –20 °C from thf/Et_2O afforded **10** as colorless crystals (270 mg, 31%); m.p. 126–127 °C. ^1H NMR (CD_3CN, 25 °C): δ = 8.27–8.33 (m, 1 H, H_{ar}), 8.18–8.22 (m, 1 H, H_{ar}), 8.06–8.14 (m, 1 H, H_{ar}), 7.82–7.95 (m, 5 H, H_{ar}), 7.55–7.69 (m, 12 H, H_{ar}), 7.38–7.42 (m, 4 H, H_{ar}), 2.94–3.00 (m, 2 H, CH_2P), 2.38 (d, J_{HP} = 13.2 Hz, 3 H, CH_3P), 1.12 (td, J_{HH} = 7.4, J_{HP} = 20.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_3CN, 25 °C): δ = 142.8 (dd, J_{CP} = 11.5, 11.6 Hz, CH_{ar}), 142.2 (pseudo-t, J_{CP} = 10.6 Hz, CH_{ar}), 141.5 (pseudo-t, J_{CP} = 10.0 Hz, CH_{ar}), 136.0 (d, J_{CP} = 2.7 Hz, CH_{ar}), 135.7 (d, J_{CP} = 3.1 Hz, CH_{ar}), 135.6–136.0 (m, CH_{ar}), 134.0 (d, J_{CP} = 10.0 Hz, CH_{ar}), 133.4–133.6 (m, CH_{ar}), 133.2 (d, J_{CP} = 10.8 Hz, CH_{ar}), 130.8 (d, J_{CP} = 12.7 Hz, CH_{ar}), 130.6 (d, J_{CP} = 13.3 Hz, CH_{ar}), 124.0 (dd, J_{CP} = 7.9, 83.3 Hz, C_{ar}), 122.7 (dd, J_{CP} = 8.7, 82.0 Hz, C_{ar}), 120.7 (q, J_{CF} = 320.0 Hz, CF_3SO_3), 118.9 (d, J_{CP} = 89.3 Hz, C_{ar}), 116.7 (d, J_{CP} = 83.9 Hz, C_{ar}), 20.5 (d, J_{CP} = 51.7 Hz, CH_2), 11.6 (d, J_{CP} = 55.9 Hz, CH_3), 7.0 (d, J_{CP} = 5.5 Hz, CH_3) ppm. ^{31}P NMR (CD_3CN, 25 °C): δ = +26.3 (d, J_{PP} = 6.1 Hz), +29.7 (d, J_{PP} = 6.1 Hz) ppm. MS (ES+): *m/z* = 639.1 $[M – OTf]^+$. HRMS (ES+): calcd. for $C_{34}H_{32}O_3F_3P_2S$ $[M – OTf]^+$ 639.1499; found 639.1493.

Diphosphonium 11: Ethyl trifluoromethanesulfonate (1.90 mL, 14.5 mmol) was added to a solution of **9** (1.30 g, 2.08 mmol) in tce (12.0 mL) and the solution was then stirred for 3 d at 110 °C. After evaporation of the solvent, an oily residue was obtained. Successive washing with toluene (2 × 30 mL), and Et_2O (2 × 30 mL) followed by recrystallization at –20 °C from thf/Et_2O gave **11** as colorless crystals (770 mg, 46%); m.p. 107–108 °C. ^1H NMR (CD_3CN, 25 °C): δ = 8.20–8.26 (m, 4 H, H_{ar}), 7.83–7.86 (m, 4 H, H_{ar}), 7.50–7.69 (m, 16 H, H_{ar}), 2.73–2.80 (m, 4 H, CH_2), 1.05–1.10 (m, 6 H, CH_3) ppm. ^{13}C NMR (CD_3CN, 25 °C): δ = 141.8 (pseudo-t, J_{CP} = 10.0 Hz, CH_{ar}), 135.7 (CH_{ar}), 133.1 (d, J_{CP} = 18.5 Hz, CH_{ar}), 130.3 (d, J_{CP} = 12.5 Hz, CH_{ar}), 129.0 (d, J_{CP} = 7.7 Hz, CH_{ar}), 123.4 (dd, J_{CP} = 8.2, 81.8 Hz, C_{ar}), 120.7 (q, J_{CF} = 320.5 Hz, CF_3SO_3), 117.1 (d, J_{CP} = 84.9 Hz, C_{ar}), 19.7 (d, J_{CP} = 50.2 Hz, CH_2), 7.2 (d, J_{CP} = 4.5 Hz, CH_3) ppm. ^{31}P NMR (CD_3CN, 25 °C): δ = +30.6 ppm. MS (ES+): *m/z* = 653.1 $[M – OTf]^+$. HRMS (ES+): calcd. for $C_{35}H_{34}O_3F_3P_2S$ $[M – OTf]^+$ 653.1656; found 653.1670.

Ylides 10c and 10e: BuLi (2.5 M in hexane, 61 μL, 0.16 mmol) was added to a solution of **10** (60 mg, 0.08 mmol) in $[D_8]$thf (2.0 mL) cooled to –78 °C. Monitoring the reaction by low-temperature NMR allowed the characterization of **10c** as a mixture of stereoisomers (95:5). According to NMR spectroscopy, **10c** was slowly converted into **10e**. After evaporation of the solvent, **10e** was obtained as a white solid (31 mg, 62%).

10c: Major isomer (95%): ^1H NMR ($[D_8]$thf, –30 °C): δ = 7.92–7.80 (m, 4 H, H_{ar}), 7.67–7.62 (m, 1 H, H_{ar}), 7.62–7.50 (m, 6 H, H_{ar}), 7.42–7.36 (m, 1 H, H_{ar}), 7.36–7.26 (m, 1 H, H_{ar}), 7.26–7.17 (m, 1 H, H_{ar}), 7.17–7.05 (m, 3 H, H_{ar}), 7.02–6.88 (m, 4 H, H_{ar}), 6.88–6.81 (m, 3 H, H_{ar}), 2.72–2.83 (m, 2 H, CH_2), 1.19–1.14 (m, 3 H, CH_3), 0.43 (dd, J_{HP} = 15.0, J_{HP+} = 20.0 Hz, 1 H, CH) ppm. ^{13}C NMR ($[D_8]$thf, –30 °C): δ = 173.7 (dd, J_{CP} = 23.4, J_{CP} = 12.6 Hz, C), 169.3 (dd, J_{CP} = 17.9, J_{CP} = 17.9 Hz, C), 144.0 (d, J_{CP} = 128.3 Hz, C), 132.2 (d, J_{CP} = 10.1 Hz, 4 CH_{ar}), 131.3 (2 CH_{ar}), 131.2 (2 CH_{ar}), 131.1 (CH_{ar}), 130.5 (CH_{ar}), 130.1 (CH_{ar}), 129.7 (d, J_{CP} = 5.0 Hz, 2 CH_{ar}), 128.6 (d, J_{CP} = 11.7 Hz, CH_{ar}), 128.5 (d, J_{CP} = 11.7 Hz, CH_{ar}), 127.7 (d, J_{CP} = 8.8 Hz, CH_{ar}), 127.0 (d, J_{CP} = 15.1 Hz, CH_{ar}), 126.8 (d, J_{CP} = 15.1 Hz, CH_{ar}), 126.5 (CH_{ar}), 126.1 (d, J_{CP} = 5.0 Hz, 2 CH_{ar}), 125.1 (d, J_{CP} = 37.7 Hz, C), 123.8 (CH_{ar}), 120.7 (q, J_{CF} = 320.1 Hz, CF_3SO_3), 27.2 (d, J_{CP} = 103.2 Hz, CH_2), 13.1 (dd, J_{CP+} = 113.0, J_{CP} = 167.0 Hz, CH), 8.9 (d, J_{CP} = 5.0 Hz, CH_3) ppm. ^{31}P NMR ($[D_8]$thf, –30 °C): δ = –89.8 (d, J_{PP} = 57.6 Hz, P), –1.6 (d, J_{PP} = 57.6 Hz, P^+) ppm. Minor isomer (5%): ^{31}P NMR ($[D_8]$thf, –30 °C): δ = –83.4 (d, J_{PP} = 54.7 Hz, P), +1.6 (d, J_{PP} = 54.7 Hz, P^+) ppm.

10e: M.p. >250 °C. ^1H NMR (CD_2Cl_2, 25 °C): δ = 7.70 (d, J_{HH} = 15.0 Hz, 10 H, H_{ar}), 7.67–7.61 (m, 3 H, H_{ar}), 7.57–7.48 (m, 8 H, H_{ar}), 7.44 (td, J_{HH} = 5.0, J_{HH} = 10.0 Hz, 4 H, H_{ar}), 2.48–2.42 (m, 2 H, CH_2), 2.05 (pseudo-t, $J_{HPPh3} = J_{HPPh2Et}$ = 5.0 Hz, 1 H, CH), 1.13–1.08 (m, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 133.1 (d, J_{CP} = 10.1 Hz, 6 CH_{ar}), 132.8 (d, J_{CP} = 2.5 Hz, 3 CH_{ar}), 132.4 (d, J_{CP} = 10.1 Hz, 4 CH_{ar}), 132.3 (d, J_{CP} = 2.5 Hz, 2 CH_{ar}), 129.2 (d, J_{CP} = 12.6 Hz, CH_{ar}), 120.0 (d, J_{CP} = 12.6 Hz, CH_{ar}), 127.1 (d, J_{CP} = 94.4 Hz, 2 C), 127.0 (d, J_{CP} = 94.4 Hz, 3 C), 121.0

(q, J_{CF} = 320.2 Hz, CF_3SO_3), 20.9 (d, J_{CP} = 61.6 Hz, CH_2), 5.6 (d, J_{CP} = 3.7 Hz, CH_3), –6.3 (dd, J_{CPPh3} = 122.0, $J_{CPPh2Et}$ = 124.6 Hz, C) ppm. ^{31}P NMR (CD_2Cl_2, 25 °C): δ = +24.2 (d, J_{PP} = 24.3 Hz, PPh_2Et), +19.3 (d, J_{PP} = 24.3 Hz, PPh_3) ppm. MS (ES+): *m/z* = 489.2 [M – OTf]$^+$. HRMS (ES+): calcd. for $C_{33}H_{31}P_2$ [M – OTf]$^+$ 489.1901; found 489.1901.

Ylides 11c and 11e: BuLi (2.5 M in hexane, 160 μL, 0.40 mmol) was added to a solution of **11** (160 mg, 0.20 mmol) in [D_8]thf (5 mL) cooled to –78 °C. Monitoring the reaction by low-temperature NMR allowed the characterization of **11c**. According to NMR spectroscopy, **11c** was then slowly converted into **11e**. After evaporation of the solvent, **11e** was obtained as an yellow oil (107 mg, 82%). Recrystallization at room temperature in CH_2Cl_2 gave **11e** as colorless crystals.

11c: ^{1}H NMR ([D_8]thf, –30 °C): δ = 7.84 (dd, J_{HP} = J_{HH} = 10.0 Hz, 2 H, H_{ar}), 7.80–7.74 (m, 2 H, H_{ar}), 7.65–7.49 (m, 9 H, H_{ar}), 7.38–7.35 (m, 1 H, H_{ar}), 7.31–7.27 (m, 1 H, H_{ar}), 7.21 (t, J_{HH} = 10.0 Hz, 1 H, H_{ar}), 7.15–7.05 (m, 4 H, H_{ar}), 6.90 (t, J_{HH} = 10.0 Hz, 1 H, H_{ar}), 6.81–6.76 (m, 2 H, H_{ar}), 6.23 (dd, J_{HP} = J_{HH} = 5.0 Hz, 1 H, H_{ar}), 2.98–2.90 (m, 2 H, CH_2), 1.22–1.08 (m, 3 H, CH_3), 0.87 (br. s, 3 H, CH_3) ppm. ^{13}C NMR ([D_8]thf, –30 °C): δ = 174.2 (dd, J_{CP} = 28.9, J_{CP} = 13.8 Hz, C), 163.2 (d, J_{CP} = 12.6 Hz, C), 145.1 (d, J_{CP} = 125.8 Hz, C), 133.08 (d, J_{CP} = 3.8 Hz, CH_{ar}), 132.76 (d, J_{CP} = 2.5 Hz, 2 CH_{ar}), 132.7 (d, J_{CP} = 3.8 Hz, 2 CH_{ar}), 131.6 (d, J_{CP} = 2.5 Hz, CH_{ar}), 131.2–131.4 (3 CH_{ar}), 130.5 (d, J_{CP} = 8.8 Hz, CH_{ar}), 130.1 (CH_{ar}), 129.1 (CH_{ar}), 129.0 (d, J_{CP} = 10.1 Hz, CH_{ar}), 128.7 (d, J_{CP} = 11.3 Hz, CH_{ar}), 128.6 (d, J_{CP} = 11.3 Hz, CH_{ar}), 127.0 (d, J_{CP} = 10.1 Hz, CH_{ar}), 126.7 (d, J_{CP} = 12.6 Hz, 2 CH_{ar}), 126.3 (CH_{ar}), 126.0 (d, J_{CP} = 3.8 Hz, CH_{ar}), 125.9 (d, J_{CP} = 3.8 Hz, CH_{ar}), 124.2 (CH_{ar}), 120.7 (q, J_{CF} = 320 Hz, CF_3SO_3), 29.0 (d, J_{CP} = 74.2 Hz, CH_2), 12.6 (pseudo-t, J_{CP} = J_{CP+} = 13.8 Hz, CH_3), 9.5 (d, J_{CP} = 6.3 Hz, CH_3), 5.7 (dd, J_{CP+} = 120.0, J_{CP} = 172.0 Hz, C) ppm. ^{31}P NMR ([D_8]thf, –30 °C): δ = +10.1 (d, J_{PP} = 94.2 Hz, P^+), –88.3 (d, J_{PP} = 94.2 Hz, P) ppm.

11e: ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.72–7.62 (m, 5 H, H_{ar}), 7.60–7.50 (m, 20 H, H_{ar}), 2.09–2.00 (m, 2 H, CH_2), 1.83 (pseudo-t, J_{HPPh3} = $J_{HPPh2Et}$ = 15.0 Hz, 3 H, CH_3), 1.07 (td, J_{HH} = 5.0, J_{HP} = 20.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 134.1 (d, J_{CP} = 10.1 Hz, CH_{ar}), 133.7 (d, J_{CP} = 8.8 Hz, CH_{ar}), 133.4 (d, J_{CP} = 3.8 Hz, CH_{ar}), 133.0 (d, J_{CP} = 2.5 Hz, CH_{ar}), 132.4 (d, J_{CP} = 8.8 Hz, CH_{ar}), 131.0 (d, J_{CP} = 12.6 Hz, CH_{ar}), 129.5 (d, J_{CP} = 13.8 Hz, CH_{ar}), 129.4 (d, J_{CP} = 13.8 Hz, CH_{ar}), 120.7 (q, J_{CF} = 320.4 Hz, CF_3SO_3), 20.7 (d, J_{CP} = 60.4 Hz, CH_2), 15.6 (t, J_{CP} = 3.8 Hz, CH_3), 7.4 (d, J_{CP} = 5.0 Hz, CH_3), –2.0 (br. s, C) ppm. ^{31}P NMR (CD_2Cl_2, 25 °C): δ = +28.83 (d, J_{PP} = 53.7 Hz, PPh_2Et), +25.39 (d, J_{PP} = 53.7 Hz, PPh_3) ppm. MS (ES+): *m/z* = 503.2 [M]$^+$. HRMS (ES+): calcd. for $C_{34}H_{33}P_2$ [M]$^+$ 503.2071; found 503.2057.

Diphosphonium 13: Methyl trifluoromethanesulfonate (1.60 mL, 14.50 mmol) was added to a solution of **12** (2.98 g, 6.59 mmol) in CH_2Cl_2 (75.0 mL) at –50 °C. The suspension was then warmed to room temperature and stirred for 2 h. After evaporation of the solvent, the crude residue was washed with Et_2O (30 mL) to afford **13** as a white solid (4.33 g, 86%). Recrystallization at –20 °C from CH_2Cl_2/pentane gave **13** as colorless crystals; m.p. 160–163 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.94–7.90 (m, 2 H, H_{ar}), 7.89–7.85 (m, 1 H, H_{ar}), 7.84–7.80 (m, 8 H, H_{ar}), 7.77–7.72 (m, 4 H, H_{ar}), 7.68–7.62 (m, 9 H, H_{ar}), 2.95 (d, J_{HH} = 13.8 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 139.3 (pseudo-t, J_{CP} = 12.2, J_{CP} = 12.5 Hz, CH_{ar}), 138.3 (dd, J_{CP} = 3.9, J_{CP} = 11.5 Hz, CH_{ar}), 135.2 (4 CH_{ar}), 133.6 (d, J_{CP} = 11.4 Hz, CH_{ar}), 131.2 (t, J_{CP} = 12.4 Hz, CH_{ar}), 130.4 (d, J_{CP} = 13.7 Hz, 8 CH_{ar}), 122.9 (dd, J_{CP} = 13.2, J_{CP} = 89.9 Hz, 2 C), 120.6 (q, J_{CF} = 320.2 Hz, CF_3SO_3), 118.0 (d, J_{CP} = 89.0 Hz, 4 C), 8.66 (d, J_{CP} = 57.7 Hz, 2 CH_3) ppm. ^{31}P NMR ($CDCl_3$, 25 °C): δ = +22.5 ppm. MS (ES+): *m/z* = 625.1 [M – OTf]$^+$. HRMS (ES+): calcd. for $C_{33}H_{30}O_3F_3P_2S$ [M – OTf]$^+$ 625.1370; found 625.1343.

Bis-Ylide 14: BuLi (2.5 M in hexane, 0.44 mmol, 180 μL) was added to a solution of **13** (170 mg, 0.22 mmol) in [D_8]thf (4.0 mL) at –78 °C. Monitoring the reaction by low-temperature NMR allowed the characterization of bis-ylide **14**. ^{1}H NMR ([D_8]thf, –60 °C): δ = 7.89 (s, 1 H, H_{ar}),7.85 (d, J_{HH} = 10.0 Hz, 2 H, H_{ar}), 7.63 (d, J_{HH} = 10.0 Hz, 8 H, H_{ar}), 7.57 (t, J_{HH} = 10.0 Hz, 1 H, H_{ar}), 7.52 (t, J_{HH} = 10.0 Hz, 4 H, H_{ar}), 7.44 (t, J_{HH} = 10.0 Hz, 8 H, H_{ar}), 0.09 (d, J_{HP} = 7.5 Hz, 4 H, CH_2) ppm. ^{13}C NMR ([D_8]thf, –60 °C): δ = 135.4 (d, J_{CP} = 20.3 Hz, 2 CH_{ar}), 135.1 (dd, J_{CP} = 79.1, J_{CP} = 9.56 Hz, 2 C), 134.0 (d, J_{CP} = 10.2, J_{CP} = 2.4 Hz, 2 CH_{ar}), 133.4 (d, J_{CP} = 86.8 Hz, 4 C), 132.0 (d, J_{CP} = 10.1 Hz, 8 CH_{ar}), 130.9 (4 CH_{ar}), 128.3 (d, J_{CP} = 11.3 Hz, 8 CH_{ar}), 128.2 (C), –5.9 (d, J_{PC} = 98.1 Hz, CH_2) ppm. ^{31}P NMR ([D_8]thf, –60 °C): δ = +19.6 ppm.

Rhodium Complex 15: A solution of [$Rh(cod)_2^+$][OTf^-] (67 mg, 0.13 mmol) in thf was added to a solution of **14** (104 mg, 0.22 mmol) in thf (3.0 mL) at –70 °C and the suspension was then stirred for 20 min. After warming to –30 °C, carbon monoxide was bubbled through the solution for 10 min. After filtration, the solvent was evaporated under vacuum. The remaining residue was washed with pentane (5.0 mL) and then extracted with CH_2Cl_2 (5.0 mL) at 0 °C to afford **15** as an orange solid (83 mg, 60%). ^{1}H NMR (CD_2Cl_2, –10 °C): δ = 7.75–7.39 (m, 24 H, H_{ar}), 1.96 (br. d, J_{HP} = 10.0 Hz, 4 H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, –10 °C): δ = 186.3 (d, J_{CRh} = 20.3 Hz, CO), 139.9 (br. s, C), 139.1 (br. s, C), 135.3 (CH_{ar}), 133.6 (CH_{ar}), 133.5–133.0 (m, CH_{ar}), 130.6–130.3 (m, CH_{ar}), 129.4 (d, J_{CP} = 12.6 Hz, CH_{ar}), 128.7 (d, J_{CP} = 12.6 Hz, CH_{ar}), 128.6 (CH_{ar}), 120.2 (q, J_{CF} = 320.1 Hz, CF_3SO_3), 1.2 (dd, J_{CP} = 40.3, J_{CRh} = 21.5 Hz, CH_2) ppm. ^{31}P NMR (CD_2Cl_2, –10 °C): δ = +35.6 (br. s) ppm. ^{103}Rh NMR (CD_2Cl_2, –10 °C): δ = +477 ppm. MS (ES+): *m/z* = 633.1 [M]$^+$. IR (CH_2Cl_2): $\tilde{\nu}$ = 2053 (CO), 1983 (CO) cm^{-1}.

Crystal Structure Determination of Compounds 10, 11, 11e, and 13

Intensity data were collected at low temperature on three different diffractometers (Bruker Apex2, Bruker Apex2 Quazar, and Agilent Gemini). Structures were solved by direct methods using SIR92[15] and refined by full-matrix least-squares procedures using the programs of CRYSTALS[16] or WINGX.[17] Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[18] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using a riding model. Absorption corrections were introduced by using the program MULTISCAN.[19]

Crystal Data for 10: $C_{33}H_{32}P_2{\cdot}2(CF_3O_3S){\cdot}C_4H_8O$, *M* = 860.81 g mol^{-1}, monoclinic, *a* = 10.4034(3), *b* = 8.9863(2), *c* = 21.4353(6) Å, β = 97.0880(10)°, *V* = 1988.63(9) Å^3, *T* = 180 K, space group *Pc*, *Z* = 2, μ(Mo-K_α) = 0.291 mm^{-1}, 57469 reflections measured, 14843 unique (R_{int} = 0.029), 11497 reflections used in the calculations [$I > 3\sigma(I)$], 506 parameters, *R* = 0.0419, wR_2 = 0.0460, Flack parameter: 0.02(4).

Crystal Data for 11: $C_{34}H_{34}P_2{\cdot}2(CF_3O_3S){\cdot}CH_2Cl_2$, *M* = 887.64 g mol^{-1}, monoclinic, *a* = 9.6404(9), *b* = 16.7750(15), *c* = 25.213(2) Å, β = 103.792(5)°, *V* = 3959.8(6) Å^3, *T* = 193 K, space group $P2_1/c$, *Z* = 4, μ(Mo-K_α) = 0.423 mm^{-1}, 29237 reflections measured, 7216 unique (R_{int} = 0.044), 5094 reflections used in the calculations [$I > 2\sigma(I)$], 605 parameters, *R* = 0.0541, wR_2 = 0.1278.

Crystal Data for 11e: $C_{34}H_{33}P_2{\cdot}CF_3O_3S$, *M* = 652.65 g mol^{-1}, triclinic, *a* = 9.9459(2), *b* = 11.2494(3), *c* = 15.1467(4) Å, *a* =

72.500(2), β = 89.6428(19), γ = 79.3817(19)°, V = 1586.40(7) Å^3, T = 180 K, space group $P\bar{1}$, Z = 2, μ(Cu-K_α) = 2.308 mm^{-1}, 29049 reflections measured, 4780 unique (R_{int} = 0.027), 4619 reflections used in the calculations [$I > 3\sigma(I)$], 452 parameters, R = 0.0353, wR_2 = 0.0468.

Crystal Data for 13: $C_{32}H_{30}P_2{\cdot}2(CF_3O_3S)$, M = 774.64 g mol^{-1}, monoclinic, a = 15.479(5), b = 13.374(5), c = 19.291(5) Å, β = 106.112(5)°, V = 3837(2) Å^3, T = 180 K, space group $P2_1/n$, Z = 4, μ(Mo-K_α) = 0.292 mm^{-1}, 42662 reflections measured, 9493 unique (R_{int} = 0.054), 5777 reflections used in the calculations [$I > 2\sigma(I)$], 453 parameters, R = 0.0553, wR_2 = 0.1341.

Acknowledgments

In addition to the Ministère de l'Enseignement Supérieur de la Recherche et de la Technologie, the Université Paul Sabatier, and the Centre National de la Recherche Scientifique (CNRS), thanks are due to the Agence Nationale de la Recherche (ANR) program (ANR-08-JCJC-0137-01) for a doctoral fellowship to C. M. Laure Vendier and Sonia Ladeira for X-ray structure determination and Christian Bijani for NMR measurements are also gratefully acknowledged. The authors also thank one of the referees for a relevant suggestion in the analysis of the steric strain in the diphosphoniums **5**, **10**, and **11**.

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Received: April 21, 2012
Published Online: ■

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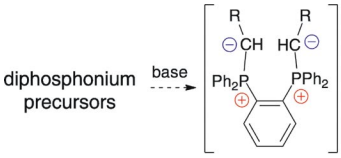

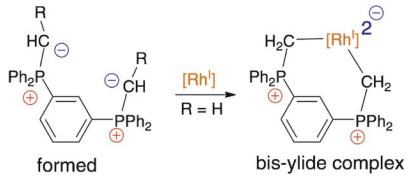

Although disubstituted *o*-phenylene-diphosphonium bis-ylides cannot be generated by double deprotonation, a *m*-phenylene isomer could and was used as a chelating electron-rich C_2 ligand in a rhodium(I) complex.

Keywords: Ylides / Ylide ligands / Phosphorus / Rhodium / Electrostatic interactions

