Oxidative Addition of Benzyliminium Tetraphenylborate to Pd(dba)(dppe): Synthesis and Catalytic Activity of [(dppe)Pd(dba)-{η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$

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The synthesis and catalytic activity of the new dicationic Pd^{II} complex [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$ from the Pd^0 complex Pd(dba)(dppe) and [$(PhCH_2)HN{=}CMe_2$]BPh_4 are described. [$(PhCH_2)HN{=}CMe_2$]BPh_4 adds to Pd(dba)(dppe) under mild conditions through a selective N–H activation. The resulting species further reacts with [$(PhCH_2)HN{=}CMe_2$]BPh_4 and generates *N*-benzyl-*N*-isopropylamine and [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$. The latter catalyzes the dimerization of methyl acrylate (MA) and the co-oligomerization of MA with styrene. Significant changes of the selectivity in the dimerization of MA have been found, e.g. changing the solvent from methyl acrylate (mostly tail-to-tail, T-T, coupling) to the ionic liquid [bmim]BF_4 (T-T and head-to-tail, H-T, coupling).
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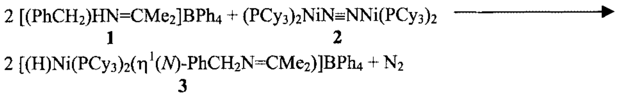
Introduction

We have recently reported that [$(PhCH_2)HN{=}CMe_2$]BPh_4 (**1**)[1] oxidatively adds to $(PCy_3)_2NiN{\equiv}NNi(PCy_3)_2$ (**2**)[2] through a selective N−H activation,[3] affording [*trans*-(H)$Ni(PCy_3)_2${η^1(*N*)-$PhCH_2N{=}CMe_2$}]BPh_4 (**3**) [Equation (1)].



$$2\,[(PhCH_2)HN{=}CMe_2]BPh_4 + (PCy_3)_2NiN{\equiv}NNi(PCy_3)_2 \xrightarrow{293\ K,\ THF,\ N_2} 2\,[(H)Ni(PCy_3)_2(\eta^1(N)\text{-}PhCH_2N{=}CMe_2)]BPh_4 + N_2 \qquad (1)$$

1, 2, 3

Compound **3** promotes the head-to-tail (H-T) oligomerization of methyl acrylate (**4**), with 100% selectivity, to give dimethyl 2-methyleneglutarate (**5**), accompanied by traces of the trimer 2,4,6-tris(methoxycarbonyl)-1-hexene (**6**), which is still an H-T coupling product.[4] Conversely, $(CH_2{=}CHCH_2NH_3)BPh_4$ (**7**)[1] adds to Ni^0 complexes, such as **2**[3] or $(PCy_3)_2Ni(\eta^2\text{-}CO_2)$ (**8**),[5] through the selective activation of the C−N allyl bond, affording [$(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)$]$BPh_4$ (**9**).[4] Compound **9**, in the presence of dihydrogen (0.1 MPa) as a cocatalyst, shows the same 100% selectivity towards the H-T oligomerization of **4**, affording **5**.[4] As we have demonstrated, in both cases the formation of (hydrido)Ni species is the key factor for catalysis to occur. In order to ascertain if such a reaction also occurs with other metal systems, we have investigated the reaction of **1** with [1,2-bis(diphenylphosphanyl)ethane][(*E*,*E*)-dibenzylideneacetone]palladium (**10**) and found a completely different behavior with respect to Ni^0. Compound **1** reacts with **10** in a multistep reaction, giving the dicationic Pd^{II} complex [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$ (**11**), that has been proved to catalyze the dimerization of **4** and the co-oligomerization of **4** with styrene (**12**). The reaction takes place in either the neat monomer(s), or in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) (**13**),[6,7] but with different yields and selectivities (Figure 1).

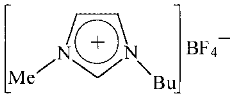


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Figure 1. 1-Butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF_4 (**13**)

The interest in ionic liquids, such as [bmim]BF_4, as solvents in biphasic processes such as Pd-catalyzed oligomerization, hydroformylation and hydrogenation of olefins is growing.[8,9] Most Pd complexes are perfectly stable and soluble in these solvents. Moreover, biphasic systems allow for easier product isolation and catalyst recycling.

Results and Discussion

Reaction of Pd(dba)(dppe) (10) with [$(PhCH_2)HN{=}CMe_2$]BPh_4 (1)

The iminium salt **1** reacts with the palladium(0) species Pd(dba)(dppe) (**10**), in THF at 293 K, to give the dicationic

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Pd^{II} complex **11** [Equation (2)] as ultimate product. This implies a different reaction pathway to that of the addition of **1** to Ni^0 [Equation (1)].

$$\underset{\mathbf{1}}{2\,[(PhCH_2)HN{=}CMe_2]BPh_4} + \underset{\mathbf{10}}{Pd(dba)(dppe)} \xrightarrow{293\ K,\ THF,\ N_2} \underset{\mathbf{11}}{[(dppe)Pd(dba)(\eta^1(N)\text{-}PhCH_2N{=}CMe_2)](BPh_4)_2} + \underset{\mathbf{20}}{(PhCH_2)HN(CHMe_2)} \tag{2}$$

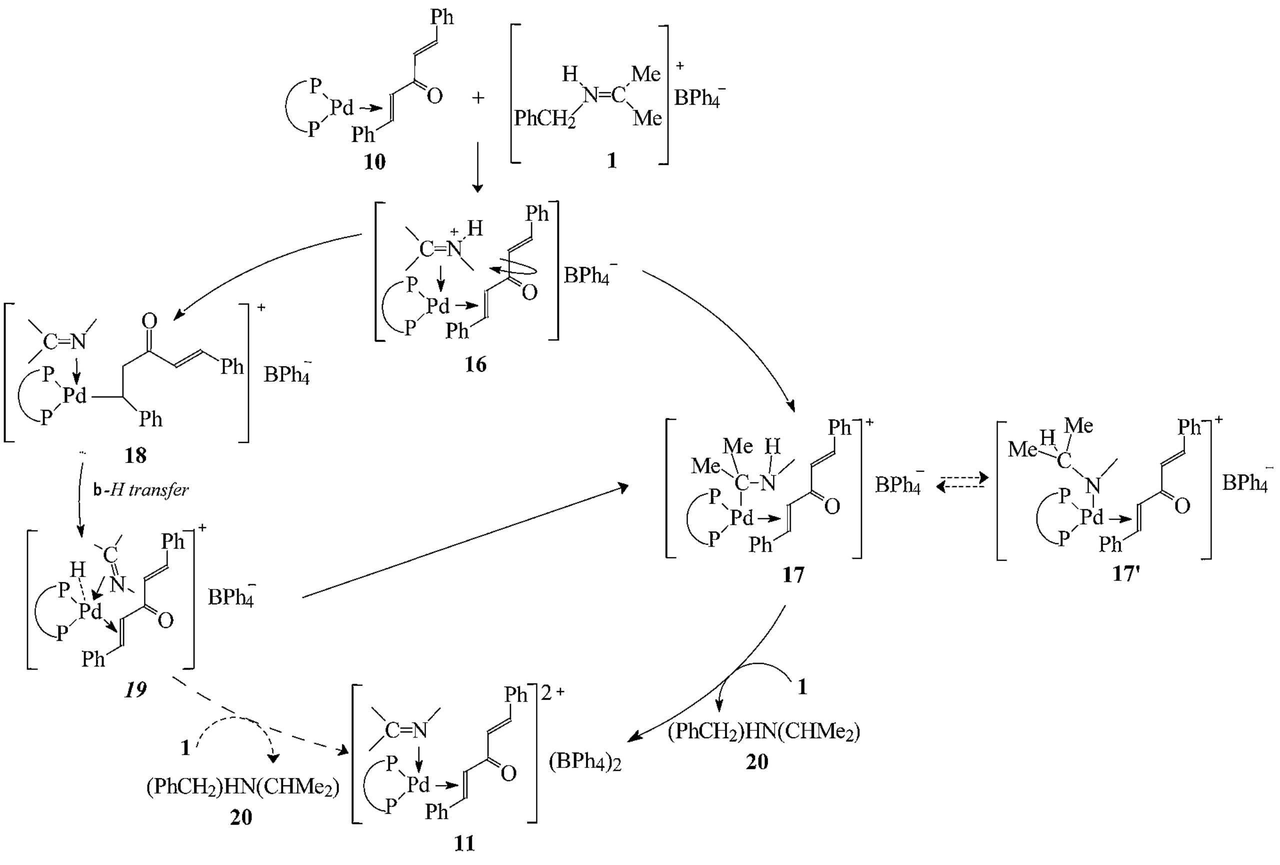
It is known that **10** exists in solution in equilibrium with a small amount of (S)Pd(dppe) (**10′**) (S = solvent) and dba. Compound **10′** undergoes the oxidative addition of reagents such as chloroform (**14**)[10] and phenyl iodide (**15**).[11] Pd(dba)(dppe) also reacts; however, the reaction is slower than that of (S)Pd(dppe). The result is the formation of a Pd^{II} species, with the release of dba [Equations (3) and (4)].

$$Pd(dba)(dppe) + CHCl_3 \rightarrow Pd(dppe)(Cl)(CHCl_2) + dba \tag{3}$$

$$Pd(dba)(dppe) + PhI \rightarrow PhPdI(dppe) + dba \tag{4}$$

In order to ascertain if **11** is formed by an initial addition of **1** to Pd^0 with the formation of a hydride species, we have continuously monitored the reaction depicted in Equation (2) by ^{1}H NMR spectroscopy at 293 K, over a period of 1 h (Scheme 1).

The iminium tetraphenylborate salt (**1**) does not add to the metal center, as observed with the Ni^0 complexes.[3] As a matter of fact, neither hydrides nor free dba have been detected during the reaction. This excludes the complication added by the presence of **10′** in the addition process. It seems that both the presence of dba as a potential proton acceptor and the lower stability of the palladium hydride species with respect to Ni[3,12b] and Pt,[12] may favor a different reaction path for Pd. Rarely have Pd−H species been isolated,[13] and often the formation of cationic (hydrido)Pd compounds have been inferred on the basis of the products that can originate by H-transfer.[14,15] Recently, we have reported that **1** reacts with Pd(dppe)$_2$ (**21**) to afford the unstable hydride [HPd(dppe)$_2$]BPh$_4$ (**22**), which has been detected in solution and characterized by ^{1}H (quint at δ = −7.37 ppm) and ^{31}P NMR spectroscopy (d at δ = 32.98 ppm).[15] The reaction of **1** with Pd(dba)(dppe) (**10**) was monitored by ^{1}H NMR spectroscopy. Soon after the addition of **1** to Pd(dba)(dppe) (**10**), a new resonance signal appears at δ = 4.75 ppm, which is assigned to an N−H moiety (**16** or **17**), as demonstrated by D$_2$O exchange. In principle, either the protonation of dba may occur to give **18** or the organometallic species **17** (possibly in equilibrium with the amido complex **17′**), derived from the coordination of the iminium cation to the palladium atom. The appearance of a new signal at δ = 2.65 ppm seems to support the



Scheme 1. The lifetime of **19** is not long enough to record the ^{1}H NMR spectrum

formation of **18**. This assignment agrees well with the ^{1}H resonance of alkyl moieties bonded to Pd {such as those in cationic complexes of the type [(N−N)Pd(CH$_3$)(acetonitrile)]BF$_4$} that commonly fall in the δ = 2.32−2.71 ppm range (CD$_3$CN, 293 K).[16] Compound **18** can be converted into **17** (or **17′**), probably through the formation of the unstable palladium hydride species (**19**), not observed by ^{1}H NMR spectroscopy. Compound **17** (or **17′**) can easily be protonated by the benzyliminium salt **1** affording the saturated amine *N*-benzyl-*N*-isopropylamine (**20**), which is found free in solution as revealed by GC-MS analysis, and the final complex **11**, in which dba is π-coordinated to the palladium atom, as suggested by two broad resonances at δ = 4.77 and 5.98 ppm, assigned to the nonequivalent protons of the C=C double bond.[10] Therefore, both Pd(dba)(dppe) and Pd(dppe)$_2$ react with the iminium salt **1**, affording the saturated amine **20** and a dicationic Pd^{II} complex, but by a different reaction path.[15] The ^{31}P NMR spectrum of the isolated complex **11** at 293 K shows that the two original resonances at δ = 34.79 and 37.07 ppm, characteristic of the asymmetric complex Pd(dba)(dppe), shift downfield and are found at δ = 35.31 and 38.00 ppm, respectively. The observed shift agrees with the greater electrophilicity of the metallic center that is oxidized to Pd^{II} after the reaction occurs. During the reaction such signals appear as broad resonances as a result of the dynamic behavior of the system Pd(dba)(dppe)/[(PhCH$_2$)HN=CMe$_2$]BPh$_4$ in solution. Unfortunately, solubility properties do not allow a low-temperature investigation. Complex **11** is stable in solution at 293 K, while above 353 K it decomposes to give benzene (**23**), generated from the BPh$_4^-$ moiety, as already observed with rhodium[17a] and nickel[4] complexes. The cleavage of the B−C bond may be promoted by the preliminary coordination of the tetraphenylborate unit to the metal atom through one of its phenyl rings. However, **23** can also be formed by the direct protolysis of one of the B−C bonds of BPh$_4^-$ by the iminium cation [Equation (5)]. The latter reaction has been proved to occur when the benzyliminium tetraphenylborate is heated in a solvent in the absence of any metal system.[17b]

$$H^+ + BPh_4^- \rightarrow BPh_3 + PhH \qquad (5)$$

We have used **11** as a catalyst in the oligomerization of methyl acrylate (**4**) and discovered that the different properties and reactivity of the system Pd(dba)(dppe)/[(PhCH$_2$)HN=CMe$_2$]BPh$_4$, relative to the nickel complexes, greatly modifies the catalytic activity towards **4**.

Catalytic Activity of 11 in the Dimerization of Methyl Acrylate (4)

Interest in the dimerization of methyl acrylate (**4**) arises from the utility, at an industrial level, of the products that can be formed by C$_3$−C$_3$ or C$_3$−C$_2$ coupling (Figure 2).

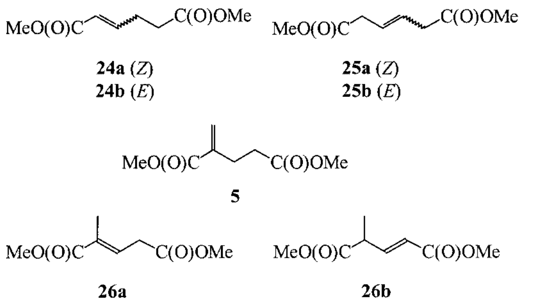
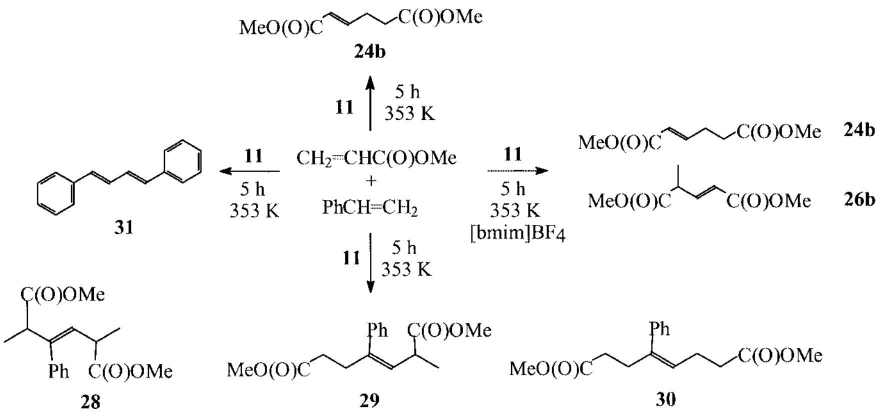


Figure 2. Tail-to-tail (**24a−b**, **25a−b**) and head-to-tail (**5**, **26a−b**) dimers of methyl acrylate

The dimethyl (*Z*)- and (*E*)-hex-2-enedioates (**24a**, **24b**), and dimethyl (*Z*)- and (*E*)-hex-3-enedioates (**25a**, **25b**), obtained by C$_3$−C$_3$ coupling of two methyl acrylate units,[18] are used principally as precursors for the synthesis of adipic acid, which is used in the Nylon-6,6 production. Conversely, head-to-tail dimers dimethyl 2-methyleneglutarate (**5**) and dimethyl methylpentenedioates (**26a**, **26b**), obtained by C$_3$−C$_2$ coupling of two methyl acrylate units, find their application essentially as monomers in co-polymerization reactions.[19] As mentioned above, in a recent study[4] we have shown that **3**[1] and **9**,[4] in the presence of H$_2$ as a cocatalyst, catalyze the selective (100%) H-T oligomerization of **4** giving dimer **5** and traces of trimer **6**. We have now studied the catalytic activity of complex **11**; typically, a **4**/**11** ratio of 1000:1 was used either in methyl acrylate as the solvent or in the ionic liquid [bmim]BF$_4$. We have found that the solvent drives both the rate of conversion and the selectivity of the process towards the T-T dimer dimethyl (*E*)-hex-2-enedioate (**24b**). The conversion yield of methyl acrylate in [bmim]BF$_4$ is four times higher than in methyl acrylate as the solvent. In [bmim]BF$_4$, **11** catalyzes the formation of the T-T product dimethyl (*E*)-hex-2-enedioate (**24b**) (41%), followed by the H-T product dimethyl 4-methylpent-2-enedioate (**26b**) (36%). Minor amounts of T-T dimers dimethyl (*Z*)-hex-2-enedioate (**24a**) (4%) and dimethyl (*E*)-hex-3-enedioate (**25b**) (5%), and the H-T dimers dimethyl 2-methyleneglutarate (**5**) (4%) and dimethyl 2-methylpent-2-enedioate (**26a**) (10%) were also obtained. In methyl acrylate, **11** catalyzes the dimerization of **4** affording the T-T dimer dimethyl (*E*)-hex-2-enedioate (**24b**) with a selectivity of 82%. Smaller amounts of the T-T dimer dimethyl (*E*)-hex-3-enedioate (**25b**) (2%) and the H-T dimers dimethyl 2-methyleneglutarate (**5**) (5%), dimethyl 2-methylpent-2-enedioate (**26a**) (9%) and dimethyl 4-methylpent-2-enedioate (**26b**) (2%) were also obtained. In both cases, traces of methyl 3-phenyl-2-propenoate (**27**) are also formed that are produced by the reaction of the phenyl moiety, formed by thermal degradation of complex **11**, with **4**. The trend shown by Pd catalysts is quite different from that characteristic of analogous Ni complexes. It has been proved[4] that the H-T coupling of **4** requires a hydride catalyst[4,20] or monodentate phosphorus ligands.[21] In the present case, the instability of Pd−H represses H-T coupling



Scheme 2

and favors the formation of T-T dimers of **4** that do not require M−H species.[18k] Also the nature of the solvent can favor or disfavor the formation of Pd−H systems and, thus, promote or prevent H-T coupling.

Catalytic Activity of 11 in the Co-Oligomerization of Methyl Acrylate (4) with Styrene (12)

Complex **11** has also been found to be active in the co-oligomerization of **4** with **12** (**11**/**4**/**12** = 1:1000:1000), when both the monomers are used as the solvent, or in [bmim]BF_4. The reaction affords the co-trimers dimethyl 2,5-dimethyl-3-phenylhex-3-enedioate (**28**), dimethyl 2-methyl-4-phenylhept-3-enedioate (**29**) and dimethyl 4-phenyloct-4-enedioate (**30**) (Scheme 2).

These co-oligomerization products are accompanied by the dimers of **4**, dimethyl (*E*)-hex-2-enedioate (**24b**) and dimethyl 4-methylpent-2-enedioate (**26b**) in the presence of [bmim]BF_4, or dimethyl (*E*)-hex-2-enedioate (**24b**) in methyl acrylate and styrene as the solvents. In each case, the dimer of styrene 1,4-diphenyl-1,3-butadiene (**31**) is also formed in traces. In [bmim]BF_4, the conversion of methyl acrylate is higher than in the neat reagents as the solvent, but the **4**/**12** co-trimers are present in minor amounts and the dimers of **4** are the major products. However, when the reagents methyl acrylate and styrene are used as the solvent, **4**/**12** co-trimers are predominantly formed. These results agree with those reported in the literature[22] that showed that the co-dimerization of **12** with **4**, catalyzed by $[Pd(C_6H_5CH{=}CH_2)Cl_2]_2$, gives the co-dimers of **12** and **4**, and the dimers of **4** or **12**. Ethylbenzene (**32**) is also formed in traces, which is produced by H-transfer to **12**, as a result of the reductive coupling of two units of **12** which gives 1,4-diphenyl-1,3-butadiene (**31**) that is found in the reaction medium. Small amounts of methyl 3-phenyl-2-propenoate (**27**) and stilbene (**33**) are also generated, most likely by the reaction of the phenyl moiety, a thermal degradation product of **11**, with **4** or **12**.[17]

Conclusions

$[(PhCH_2)HN{=}CMe_2]BPh_4$ (**1**) reacts with palladium(0) complex Pd(dba)(dppe) (**10**) to afford the dicationic Pd^{II} complex $[(dppe)Pd(dba)\{\eta^1(N)\text{-}PhCH_2N{=}CMe_2\}](BPh_4)_2$ (**11**), through a complex path that starts with the protonation of the coordinated dba. Complex **11** has been proved to be catalytically active in the dimerization of methyl acrylate (**4**) and in the co-oligomerizations of **4** with styrene (**12**). No polymerization products have been observed. In neat methyl acrylate, the selective (84%) T-T coupling of **4** affording dimethyl (*E*)-hex-2-enedioate (**24b**) with a regioselectivity of 82% has been observed. In the ionic liquid [bmim]BF_4, a selectivity of 50% was found towards the T-T coupling of **4**, affording dimethyl (*E*)-hex-2-enedioate (**24b**). The H-T dimethyl 4-methylpent-2-enedioate (**26b**) is formed with a regioselectivity of ca. 40%. In neat methyl acrylate/styrene, co-trimers are formed in higher yields than in [bmim]BF_4, which favors the homo-coupling of **4**.

Experimental Section

General Comments: Unless otherwise stated, all reactions and manipulations were conducted under dinitrogen by using vacuum-line techniques. All solvents were dried as described in the literature[23] and stored under N_2. MA was purchased from Fluka and stored under N_2. $[(PhCH_2)HN{=}CMe_2]BPh_4$,[1] Pd(dba)(dppe)[10a,24] and [bmim]BF_4 [6,25] have been prepared as previously reported. Elemental C,H,N microanalyses were performed with an Euro EA 3000 analyser, P analyses were performed using a UV Shimadzu 1601 (λ = 460 nm), Pd was dosed using a Perkin−Elmer Atomic Absorption Spectrometer 3110. NMR spectra were run with a Varian XL-200 instrument. ^1H NMR chemical shifts are in ppm vs. TMS and referenced to the solvent peak. ^{31}P NMR chemical shifts are in ppm vs. 85% H_3PO_4. GC-MS analyses were carried out with a Shimadzu GC-17A linked to a Shimadzu GCMS-QP5050 selective mass detector (capillary column: 60 m × 0.25 mm Supelco MDN-5S, 0.25 μm film thickness). Temperature program: 343 K (3 min) → 21 min → 553 K (30 min). GC analyses were performed by using an HP 5890 Series II GC (capillary column: 30 m × 0.25 mm Altech AT-5, 0.25 μm film thickness). Temperature program: 318 K (5 min) → 7.5 min → 393 K (1 min) → 9.5 min → 583 K (30 min).

Synthesis of $[(dppe)Pd(dba)\{\eta^1(N)\text{-}PhCH_2N{=}CMe_2\}](BPh_4)_2$ (11): $[(PhCH_2)HN{=}CMe_2]BPh_4$ (0.140 g, 0.30 mmol), dissolved in THF (10 mL), was added to a solution of Pd(dba)(dppe) (0.183 g, 0.25 mmol) in THF (10 mL), prepared under dinitrogen at 293 K. The resulting mixture was stirred at room temperature (293 K) for 5 h, until its color turned to yellowish orange. The reaction mixture was filtered, concentrated in vacuo, and, after addition of diethyl ether (20 mL), cooled to 253 K. The red oil obtained was isolated, washed with diethyl ether (2 × 3 mL), dried in vacuo, and characterized as [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$ (**11**) (0.219 g, 58%). ^{1}H NMR ([D_8]THF, 293 K): δ = 2.02 (s, 3 H, $-CH_3$), 2.07 (s, 3 H, $-CH_3$), 2.50 (br. s, 4 H, $-CH_2CH_2-$), 4.42 (s, 2 H, $-CH_2$Ph), 4.77 (br. s, 1 H, $-HC{=}CH-$), 5.98 (br. s, 1 H, $-HC{=}CH-$), 6.70 (t, J_{ortho} = 7.10 Hz, 2 × 4 H, H_{para} BPh_4^-,), 6.80 (t, J_{ortho} = 7.44 Hz, 2 × 8 H, H_{meta} BPh_4^-), 6.93−7.82 (m, 53 H, 2 × 8 H, H_{ortho} BPh_4^-, $H_{ortho,meta,para}$ *Ph*CH_2-, dppe, $H_{aromatic,olefinic}$ dba) ppm. ^{31}P NMR ([D_8]THF, 293 K): δ = 35.31 (m), 38.00 (m) ppm. $C_{101}H_{91}B_2NOP_2Pd$ (1524.80): calcd. C 79.56, H 6.02, N 0.92, Pd 6.98, P 4.06; found C 79.77, H 6.05, N 1.08, Pd 6.85, P 4.07. Water must be avoided in order to prevent the hydrolysis of benzyliminium tetraphenylborate to afford acetone and benzylammonium tetraphenylborate.

Reaction of Pd(dba)(dppe) (10) with [$(PhCH_2)HN{=}CMe_2$]BPh_4 (1) Monitored by ^{1}H NMR Spectroscopy: A water-free [D_8]THF solution (0.75 mL) of Pd(dba)(dppe) (13.20 mg, 0.018 mmol), prepared under N_2, was introduced into an NMR tube, avoiding contact with air. The iminium tetraphenylborate was added (8.20 mg, 0.018 mmol), the tube sealed and the solution continuously monitored by ^{1}H NMR spectroscopy at 293 K (Scheme 1). **18:** ^{1}H NMR ([D_8]THF, 293 K): δ = 1.95 (s, 3 H, $-CH_3$), 2.05 (s, 3 H, $-CH_3$), 2.20 (br. s, 4 H, $-CH_2CH_2-$), 2.65 (br. s, Pd−alkyl), 4.43 (s, 2 H, $-CH_2$Ph), 4.75 (br. s, 1 H, N−*H*), 6.70 (t, J_{ortho} = 7.10 Hz, 2 × 4 H, H_{para} BPh_4^-), 6.80 (t, J_{ortho} = 7.44 Hz, 2 × 8 H, H_{meta} BPh_4^-), 6.93−7.82 (m, 53 H, 2 × 8 H, H_{ortho} BPh_4^-, $H_{ortho,meta,para}$ *Ph*CH_2-, dppe, $H_{aromatic,olefinic}$ dba) ppm. The formation of *N*-benzyl-*N*-isopropylamine (**20**) was confirmed by analyzing the reaction mixture by GC-MS: $C_{10}H_{15}N$: *m*/*z* = $[M]^+$ (not observed), 134, 106, 91, 77, 65, 41, 39.

Dimerization of Methyl Acrylate (4) Promoted by 11 in Methyl Acrylate: Methyl acrylate (1 mL, 11.10 mmol) was added to [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$ (13.75 mg, 0.009 mmol) under N_2. The reaction mixture was then stirred at 353 K for 5 h and, after cooling to 293 K, the products were diluted in toluene. They were analyzed by GC and GC-MS, that showed that dimethyl (*E*)-hex-2-enedioate (**24b**) was the main product (82%) and **26a** (9%), **5** (5%), **25 b** (2%) and **26b** (2%) were the minor products. **24b:** GC-MS: $C_8H_{12}O_4$: *m*/*z* = $[M]^+$ (not observed), 157 [$M^+ - CH_3$], 140 [$CH_3O(O)C{-}CH{=}CH{-}CH{-}CH_2{-}CO$], 108 [$OC{-}CH{=}CH{-}CH{=}CH{-}CO$], 97 [$H_2C{=}CH{-}CH{=}CH{-}C(O)O$], 81 [$H_2C{=}CH{-}CH{=}CH{-}CO$], 71 [$H_2C{=}CH{-}C(O)O$], 59 [$C(O)OCH_3$], 53 [$H_2C{=}CH{-}CH{=}CH$], 41 [$H_2C{=}CH{-}CH_2$], 39 [$HC{-}CH{=}CH$], 31 [$OCH_3$].

Dimerization of Methyl Acrylate (4) Promoted by 11 in [bmim]BF_4: Methyl acrylate (0.47 mL, 5.22 mmol) and the ionic liquid [bmim]BF_4 (0.25 mL) were added to [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$ (6.40 mg, 0.004 mmol) under N_2. The reaction mixture was then stirred at 353 K for 5 h and, after cooling to 293 K, the products were isolated by extraction in toluene. They were analyzed by GC and GC-MS, that showed that dimethyl (*E*)-hex-2-enedioate (**24b**) (41%) and dimethyl 4-methylpent-2-enedioate (**26b**) (36%) were the main products and **24a** (4%), **25b** (5%), **5** (4%) and **26a** (10%) were the minor products. **26b:** GC-MS: $C_8H_{12}O_4$: *m*/*z* = $[M]^+$ (not observed), 140 [$M^+ - CH_3OH$], 112 [$H_2C{=}CH{-}CH{=}CH{-}C(O)OCH_3$], 97 [$H_2C{=}CH{-}CH{=}CH{-}C(O)O$], 85 [$CH{=}CH{-}C(O)OCH_3$], 81 [$H_2C{=}CH{-}CH{=}CH{-}CO$], 71 [$H_2C{=}CH{-}C(O)O$], 59 [$C(O)OCH_3$], 53 [$H_2C{=}CH{-}CH{=}CH$], 41 [$H_2C{=}CH{-}CH_2$], 39 [$HC{-}CH{=}CH$].

Co-Oligomerization of Methyl Acrylate (4) and Styrene (12) Promoted by 11 in Methyl Acrylate and Styrene: Methyl acrylate (0.46 mL, 5.11 mmol) and styrene (0.59 mL, 5.13 mmol) were added to [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$ (6.20 mg, 0.004 mmol) under N_2. The reaction mixture was then stirred at 353 K for 5 h and, after cooling to 293 K, the products were diluted in toluene and analyzed by GC and GC-MS. Three different isomers of methyl acrylate/styrene trimers were isolated, dimethyl 2,5-dimethyl-3-phenylhex-3-enedioate (16%) (**28**), dimethyl 2-methyl-4-phenylhept-3-enedioate (14%) (**29**) and dimethyl 4-phenyloct-4-enedioate (35%) (**30**), and the dimer of methyl acrylate dimethyl (*E*)-hex-2-enedioate (32%) (**24b**). **28:** GC-MS: $C_{16}H_{20}O_4$: *m*/*z* = $[M]^+$ (not observed), 244 [$M^+ - CH_3OH$], 216 [$H_2C{=}CH{-}C(Ph){=}CH{-}CH(CH_3)C(O)OCH_3$ or $H_2C{=}CH{-}CH{=}C(Ph){-}CH(CH_3)C(O)OCH_3$], 207, 185 [$H_2C{=}CH{-}C(Ph){=}CH{-}CH(CH_3)CO$ or $H_2C{=}CH{-}CH{=}C(Ph){-}CH(CH_3)CO$], 143 [$HC{-}C(Ph){=}CH{-}CH{-}CH_3$ or $CH{-}CH{=}C(Ph){-}CH(CH_3)$], 129 ($Ph{-}C{=}CH{-}CH{=}CH_2$), 115 ($Ph{-}C{=}CH{-}CH$), 96, 77 ($C_6H_5$), 59 [$C(O)OCH_3$], 51 ($C_4H_3$). **29:** GC-MS: $C_{16}H_{20}O_4$: *m*/*z* = $[M]^+$ (not observed), 244 [$M^+ - CH_3OH$], 216 [$H_2C{=}CH{-}CH{=}C(Ph){-}CH_2{-}CH_2C(O)OCH_3$ or $H_2C{=}CH{-}C(Ph){=}CH{-}CH(CH_3)C(O)OCH_3$], 207, 185 [$H_2C{=}CH{-}CH{=}C(Ph){-}CH_2{-}CH_2CO$ or $H_2C{=}CH{-}C(Ph){=}CH{-}CH(CH_3)CO$], 143 [$HC{-}CH{=}C(Ph){-}CH_2{-}CH_2$ or $CH{-}C(Ph){=}CH{-}CH{-}CH_3$], 129 [$HC{-}CH{=}C(Ph){-}CH_2$], 115 [$HC{-}CH{=}C{-}Ph$], 96, 77 [$C_6H_5$], 59 [$C(O)OCH_3$], 51 [$C_4H_3$]. **30:** GC-MS: $C_{16}H_{20}O_4$: *m*/*z* = $[M]^+$ (not observed), 244 [$M^+ - CH_3OH$], 216 [$H_2C{=}CH{-}CH{=}C(Ph){-}CH_2CH_2C(O)OCH_3$ or $H_2C{=}CH{-}C(Ph){=}CH{-}CH_2CH_2C(O)OCH_3$], 207, 157 [$Ph{-}C{=}CH{-}CH{-}CH_2CO$], 141, 129 [$Ph{-}C{=}CH{-}CH{=}CH_2$], 115 [$Ph{-}C{=}CH{-}CH$], 88, 77 [$C_6H_5$], 59 [$C(O)OCH_3$], 51 [$C_4H_3$].

Co-Oligomerization of Methyl Acrylate (4) and Styrene (12) Promoted by 11 in [bmim]BF_4: Methyl acrylate (0.911 g, 10.58 mmol), styrene (1.028 g, 9.87 mmol) and the ionic liquid [bmim]BF_4 (1 mL) were added to [(dppe)Pd(dba){η^1(*N*)-$PhCH_2N{=}CMe_2$}]$(BPh_4)_2$ (12.30 mg, 0.008 mmol) under N_2. The reaction mixture was then stirred at 353 K for 5 h and, after cooling to 293 K, the products were isolated by extraction in toluene and analyzed by GC and GC-MS. Three different isomers of methyl acrylate/styrene trimers were isolated, dimethyl 2,5-dimethyl-3-phenylhex-3-enedioate (4%) (**28**), dimethyl 2-methyl-4-phenylhept-3-enedioate (3%) (**29**) and dimethyl 4-phenyloct-4-enedioate (16%) (**30**), and the dimers of methyl acrylate dimethyl (*E*)-hex-2-enedioate (36%) (**24b**) and dimethyl 4-methylpent-2-enedioate (25%) (**26b**).

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