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Synthesis, characterization, and reactivity of (π-allyl)palladium(II) wrap-around complexes with 1,3-dienes

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This manuscript is dedicated to our friend and colleague, Prof. Robert Bergman, whose remarkable insights, fortitude to tackle tough problems, and experimental rigor have led to numerous path-breaking advances in organometallic and organic chemistry.

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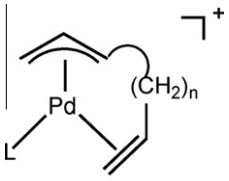
(π-Allyl)palladium(II)
pi-Allyl Pd(II)
Wrap-around complex
1,3-Diene insertion

ABSTRACT

Synthesis of a series of cationic "wrap-around" complexes, η^3-, η^2- (CH_2–CH–CHR–CH_2–CH_2–CH=CHX) Pd(II)L^+ (R = H, CH_3; X = H, Cl, CO_2Me; L = PPh_3, $P(C_4H_4N)_3$), is described. These chelate complexes were prepared by exposure of π-allyl chloride dimers, (η^3-(CH_2-CX-CH_2)PdCl)$_2$, to either 1,3-butadiene or isoprene to yield π-allyl chloride dimers of the type (η^3-CH_2CHCRCH_2CH_2CH = CH(X)PdCl)$_2$ which result from insertion of the diene into each π-allyl unit. Abstraction of chloride with either $AgSbF_6$ or $NaB(Ar_F)_4$ in the presence of L gives the cationic wrap-around complexes in high yields. Single crystal X-ray diffraction studies of **8a** (R = –CH_3, X = –Cl, L = PPh_3) and **9a** (R = –H, X = –Cl, L = PPh_3) show that Pd(II) adopts essentially a square planar geometry and the chelate arm occupies a *syn* orientation with respect to the allyl unit. Exposure of these wrap-around complexes to nitriles of differing basicities displaces the chelated alkene to varying extents and allows assessment of the relative strengths of chelation as a function of substituents, X and R. Initial rapid displacement of the chelated alkene yields a *syn*-π-allyl isomer which equilibrates with the *anti*-π-allyl isomer which cannot close to form a chelate. Treatment of **8b** with 1,3-butadiene gives not polybutadiene but 2-chloro-4-methyl-1,E-4,6-heptatriene and 2-chloro-4-methyl-1,Z-4,6-heptatriene. Formation of these trienes is first-order in butadiene. This reaction serves as a model for chain-transfer in the polymerization of butadiene.

1. Introduction

Allyl Pd(II) complexes containing a chelating olefinic group of general structure A ("wrap-around" complexes) have been formulated as key intermediates in several reactions and have been isolated and characterized by a number of groups. Complexes in which $n = 3$ have been established as intermediates in the Pd(II)-catalyzed telomerization of 1,3-butadiene (BD) in protic solvents as well as in the Pd-catalyzed carbocyclization of 1-acetoxy-2,7-dienes. In each case, complexes of type **1**, in which the anion is weakly coordinating (e.g. BF_4^-), have been isolated and shown to be competent intermediates [1–3].



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Akermark and Vitagliano showed that the cationic (η^3-geranyl)Pd(II) and (η^3-neryl)Pd(II) complexes supported by acetonitrile exist as an equilibrating mixture of three species as shown in Scheme 1, with the ratio of wrap-around complex **2** to bis-nitrile complexes **3**-*syn* and **3**-*anti*, dependent on the palladium to nitrile ratio [3]. The η^3-neryl system possessing *anti* stereochemistry does not form a chelate complex, and the authors propose the differing propensities of these systems to form chelates may explain the differing regiochemistries of nucleophilic attack on the allyl moieties.

Nickel wrap-around complexes similar in structure to **1** have played a role in Ni(II)-catalyzed diene polymerization reactions. Taube has shown that "ligand-free" wraparound Ni(II) complexes are highly reactive initiators for butadiene (BD) polymerization [4]. We have previously spectroscopically observed (allyl)Ni (η^4-butadiene)$^+$, **4**, at low temperatures and showed that this species reacts rapidly with two equivalents of BD to generate a third insertion, wrap-around complex **5** shown in Scheme 2 [5]. At higher temperatures, the third insertion product initiates polymerization of BD and intermediates in the chain growth have been identified [5,6].

Hughes and Powell studied the monomer/dimer equilibria shown below and suggested that a wrap-around complex similar to **7** may be involved in BD polymerization initiated by the nickel dimer, [(allyl)Ni(O_2CCF_3)]$_2$ (Scheme 3) [7].

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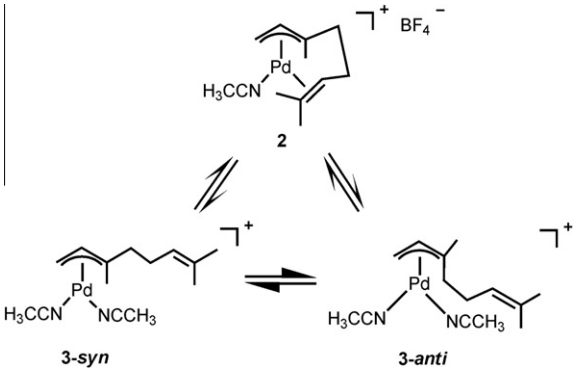
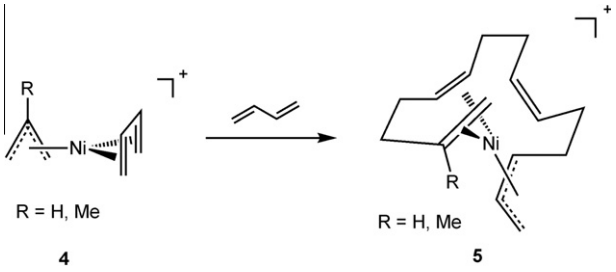
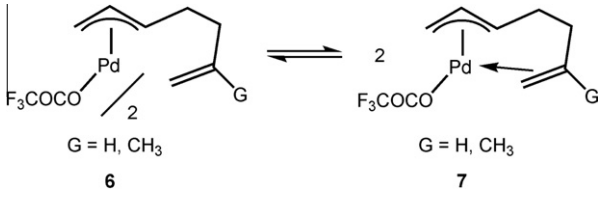


Scheme 1. Displacement of η^2-olefin chelate by nitrile.



Scheme 2. Ni(II) third insertion wrap-around complex **5**.



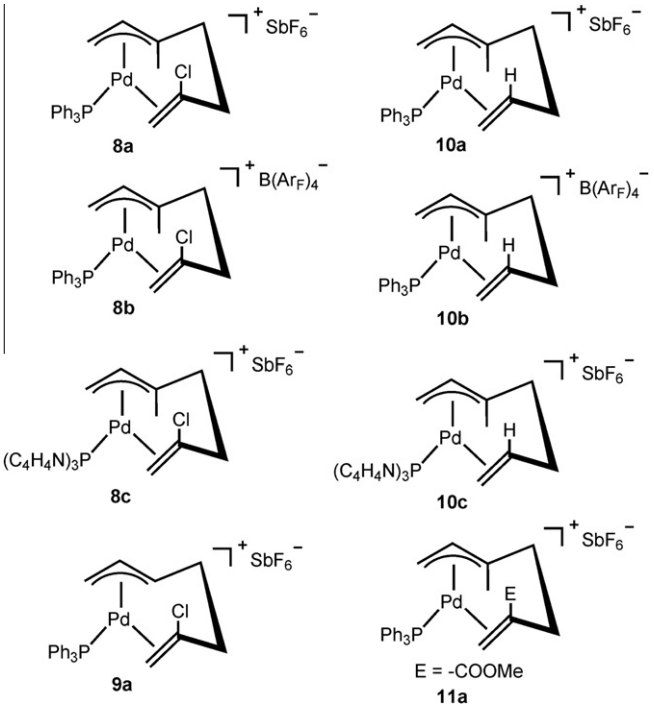
Scheme 3. Monomer/dimer equilibrium studied by Hughes et al. [7].

We report here an investigation of simple Pd(II) wrap-around complexes of type **1**, with $n = 2$. These studies include the synthesis and structural analysis of several simple derivatives of **1** and a semi-quantitative analysis of the binding strength of the chelate arm as a function of substituents on the alkene through analysis of dynamic NMR spectra. Attempted use of these systems for diene polymerization resulted in chain transfer and release of a 1,4,6-triene, suggesting that polymerization of dienes is not feasible with the Pd systems in contrast to the Ni analogs.

2. Results and discussion

2.1. Synthesis of and characterization of wrap-around complexes

The wrap-around complexes **8a**–**11a** (Scheme 4) were synthesized starting with the $[(\eta^3\text{-}H_2CC(X)CH_2)PdCl]_2$ dimer [8]. Functional groups in the 2-position of the allyl unit (X = H, Cl, COOMe) are readily incorporated by the use of the corresponding 2-substituted allyl chlorides. Selective insertion of a single diene unit forms the corresponding dimeric complexes as a 50:50 mixture of *syn* and *anti* isomers. The unsubstituted (X = H) *syn*/*anti* isomers have been previously reported [9,10]. Subsequent halide abstraction with $NaB(Ar_F)_4$ or $AgSbF_6$ at −78 °C and addition of a phosphine ligand affords the cationic *syn* wrap-around complexes in near quantitative yields (Scheme 5).



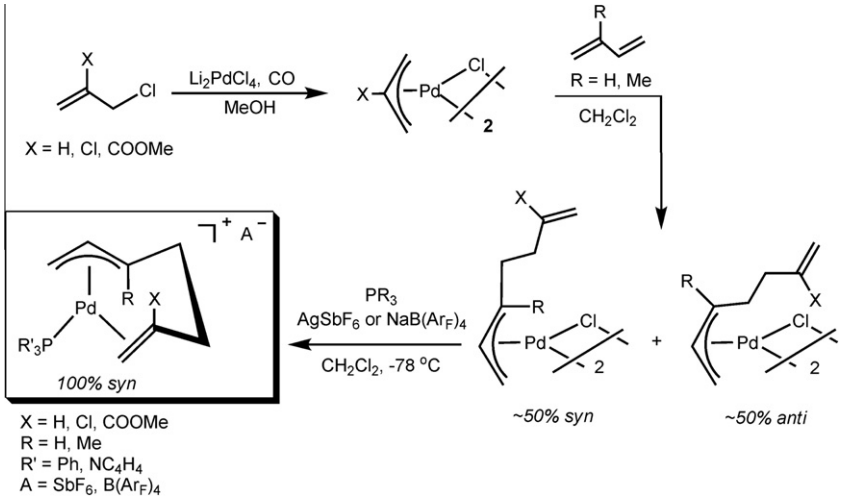
Scheme 4. Wrap-around Pd(II) complexes prepared.

The cationic, *syn* wrap-around complexes were characterized by multinuclear NMR spectroscopy and elemental analyses (see Section 4). The solid state structures of **8a** and **9a** were determined by X-ray crystallography. ORTEP drawings for **8a** and **9a** are shown in Figs. 1 and 2, respectively. The crystallographic information is reported in Tables SI.1–SI.3 in the Supporting Information. The X-ray structures confirm the *syn* geometry of the wrap-around complexes and the η^2-binding of the chelating olefin arm and are structurally similar to the geranyl chelate reported by Akermark and Vitagliano, and also by Ciajolo [3,11].

Typical ^{1}H NMR spectra for a selection of wrap-around complexes are shown in Supporting Information (Fig. SI.1). The proton spectra are similar to a wrap-around complex reported by Echavarren and co-workers [12] and signal assignments are straightforward (these assignments appear in Section 4). Signals assigned to the η^2-bound olefinic protons appear upfield of the chemical shift of the corresponding free olefins, characteristic of an alkene–metal interaction [13–15]. Additionally, low temperature NMR studies (−90 °C) of each complex verified that there were no unexpected fluxional processes occurring in these species.

2.2. Determination of olefin binding affinities by reaction of wrap-around complexes with nitrile ligands

With the cationic palladium(II) wrap-around complexes in hand, titration experiments were performed using various nitriles to displace the η^2-bound olefin. A quantitative assessment of the equilibrium between the wrap-around complexes and their nitrile adducts provides relative binding strengths of the η^2-olefins coordinated to the metal in the wrap-around complexes. The effect of varying the electronic properties of each η^2-olefin, the phosphine ligand, and the counterion were examined. The equilibrium constants were quantified by monitoring the allylic, olefinic, and methyl ^{1}H NMR resonances and also the ^{31}P NMR resonances. These results reveal how readily the chelates open and thus may offer insight into the ability of these wrap-around complexes to react with less coordinating substrates.



Scheme 5. General synthetic route for Pd(II) wrap-around complexes.

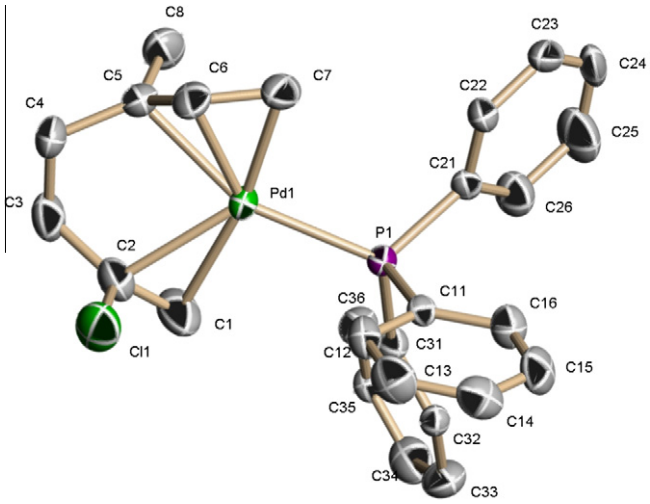


Fig. 1. ORTEP diagram of **8a**. Thermal ellipsoids drawn at 50% probability, SbF_6^- and protons omitted for clarity. Selected bond lengths (Å): Pd(1)–C(7) 2.160(5), Pd(1)–C(6) 2.183(5), Pd(1)–C(5) 2.275(5), Pd(1)–C(1) 2.294(5), Pd(1)–C(2), 2.340(5), C(1)–C(2) 1.369(8), C(5)–C(6) 1.420(8), C(6)–C(7) 1.403(8).

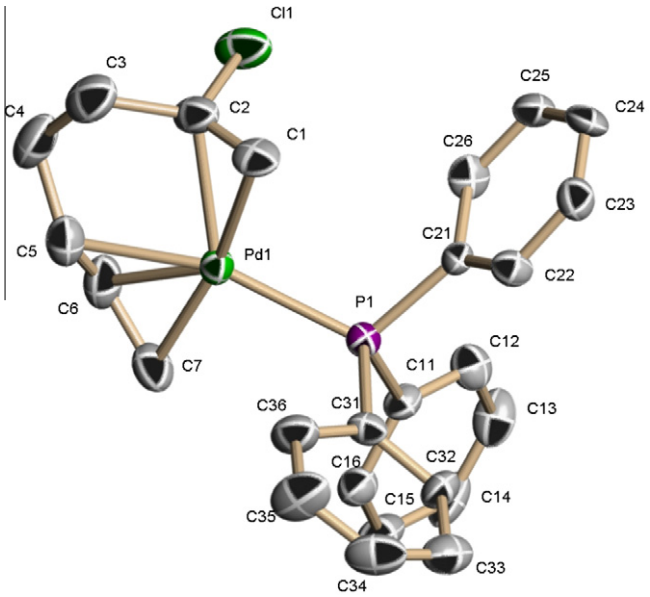
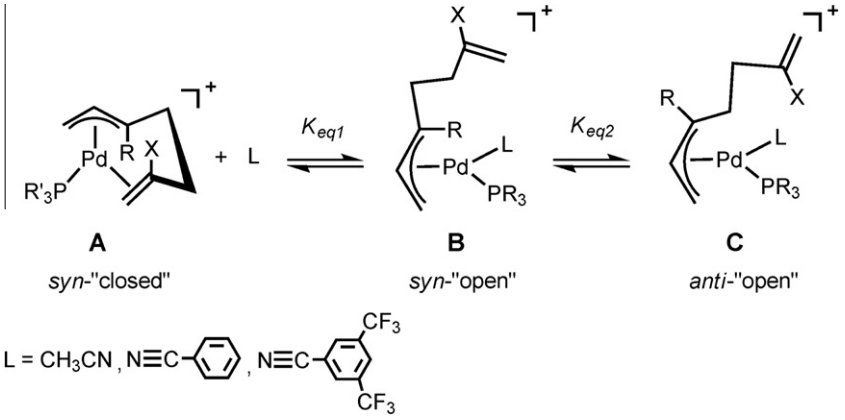


Fig. 2. ORTEP diagram of **9a**. Thermal ellipsoids drawn at 50% probability, SbF_6^- and protons omitted for clarity. Selected bond lengths (Å): Pd(1)–C(7) 2.129(7), Pd(1)–C(6) 2.156(7), Pd(1)–C(5) 2.203(7), Pd(1)–C(1) 2.326(6), Pd(1)–C(2), 2.326(7), C(1)–C(2) 1.342(10), C(5)–C(6) 1.373(12), C(6)–C(7) 1.417(11).

Upon addition of nitrile to the wrap-around complex **A**, the nitrile can displace the η^2-olefin to form the "open" complex **B**. Once the wrap-around complex is open, it can undergo *syn/anti* isomerization to form the open *anti* complex **C**, where the longer chain is *anti* to the allylic proton (H_c) (Scheme 6).

The opening/closing equilibria for these systems (interconversion of **A** and **B**) are fast on the NMR time scale and therefore only the time-averaged resonances are observed, whereas the *syn/anti* isomerization is slow on the NMR time scale and the *anti* isomer cannot form a stable wrap-around complex. This is clearly shown by the olefinic, methyl, and allylic (H_c) resonances in the ^1H NMR spectra in Fig. 3, where 0, 1, 2, 3, and 5 equivalents of 3,5-bis(trifluoromethyl)benzonitrile have been added to **8b**. First, consider the allylic central ^1H signal, H_c. At zero equivalents of nitrile, **8b** is completely closed and H_c resonates at 6.19 ppm. Upon addition of one equivalent of nitrile, the allylic resonance shifts upfield to 5.87 ppm, where this signal-averaged peak corresponds to 50:50 closed:open, or half **A** and half **B**. Subsequent additions of nitrile shift the allylic resonance further upfield until, at five equivalents of nitrile, **8b** has fully converted from closed (**A**) to open (**B**) and H_c resonates at 5.64 ppm. The equilibrium ratio of [**A**]:[**B**] can be computed from the weighted average resonance (see below). The *syn/anti* isomerization from open *syn* complex **B** to *anti*-**C**, on the other hand, is slow on the NMR time scale, and *anti*-**C** has a separate, distinct H_c allylic resonance at 5.54 ppm. As more equivalents of nitrile are added, more of the open complex **B** is formed, which then in turn isomerizes to open complex **C**. At 1, 2, and 3 equivalents of nitrile, the allylic resonance for **C** grows as more open complex is formed and isomerized, until **8b** is fully opened at five equivalents of 3,5-bis(trifluoromethyl)benzonitrile. At long times, the *syn/anti* ratio is constant and thermodynamically slightly favors the *syn* form.

A similar phenomenon is observed with the olefinic resonances. The η^2-bound olefinic protons in wrap-around complex **8b** resonate upfield at 4.73 and 4.46 ppm. Upon addition of nitrile, these olefinic protons shift downfield as the nitrile displaces the η^2-olefin and resonate at 5.17 and 5.13 ppm when full conversion to **B** is achieved. The olefinic peaks for the *anti* open isomer, **C**, resonate at 5.24 and 5.23 ppm, characteristic of resonances for an unbound



Scheme 6. Titration of wrap-around complexes with nitrile.

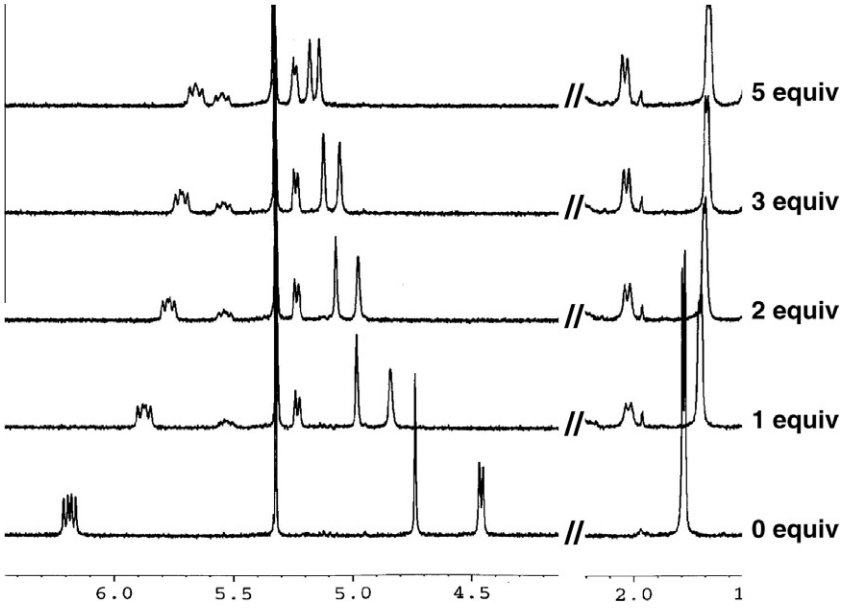


Fig. 3. Allylic, olefinic, and methyl regions of the ^{1}H NMR spectra for the titration of **8b** with 3,5-bis(trifluoromethyl)benzonitrile in CD_2Cl_2.

olefin. Finally, the methyl resonances exhibit the same behavior and resonate at 1.78 ppm for the completely closed complex **A**, 1.67 ppm for the completely open complex **B**, and 2.03 ppm for the *anti* open isomerized complex **C** for the 3,5-bis(trifluoromethyl)benzonitrile adduct.

Examination of the fast exchange between closed and open complexes **A** and **B** was possible through analysis of variable temperature ^{31}P NMR spectra recorded upon addition of 5, 10, and 20 equivalents of benzonitrile to wrap-around complex **10a**. When five equivalents of benzonitrile were added to wrap-around complex **10a**, a roughly 50/50 mixture of open and closed species was generated (Fig. 4). The phosphorus resonance at 28.1 ppm (23 °C), assigned to **C**, shifts upfield slightly to 27.6 ppm upon cooling to −80 °C. The second ^{31}P NMR peak at 27.1 ppm at room temperature, assigned to the time-averaged signal for **A** and **B**, broadens upon cooling, and decoalesces at temperatures lower than −70 °C into two separate peaks as the fast exchange between **A** and **B** is frozen out. At −80 °C, the resonance for the open complex of **10a** (**B**) is shifted downfield to 28.0 ppm. Conversely, the resonance for the closed wrap-around complex **A** shifts upfield to 26.7 ppm towards the original phosphorus shift for the completely closed wrap-around **10a**, which resonates at 26.6 ppm. While the exchange between bound and free olefin is not completely frozen out at this temperature, as evidenced by the broad peaks, it is clear that the resonance at room temperature is indeed a time-averaged signal between open and closed complexes **A** and **B**.

The equilibrium constants determined by the titration experiments (K_{eq1} for the closed/open equilibrium and K_{eq2} for the *syn*/*anti* isomerization equilibrium) can be estimated by monitoring the resonances and integrations of the allylic, olefinic, and methyl peaks in the ^{1}H NMR and the phosphorus peaks in the ^{31}P NMR for the titration experiments. Since the resonances for **A** and **B** are averaged, a weighted distribution calculation is used to determine the relative amounts of [**A**] and [**B**] (see Section 4). The concentration of **C** is easily determined since it is not rapidly equilibrating with the other isomers and yields sharp signals. From this information K_{eq1} and K_{eq2} were determined (Eq. (1)). Since K_{eq1} involves competitive binding between the η^2-olefin and the nitrile, it is related to the binding strength of the η^2-olefin. K_{eq2} represents the thermodynamic ratio between the *syn* and *anti* isomers.

$$K_{eq1} = \frac{[\mathbf{B}]}{[\text{Nitrile}][\mathbf{A}]}, \quad K_{eq2} = \frac{[\mathbf{C}]}{[\mathbf{B}]} \tag{1}$$

The titration experiments were repeated with two other nitriles, acetonitrile and benzonitrile, and the equilibrium constants for the opening of the wrap-around complex (K_{eq1}) as well as the

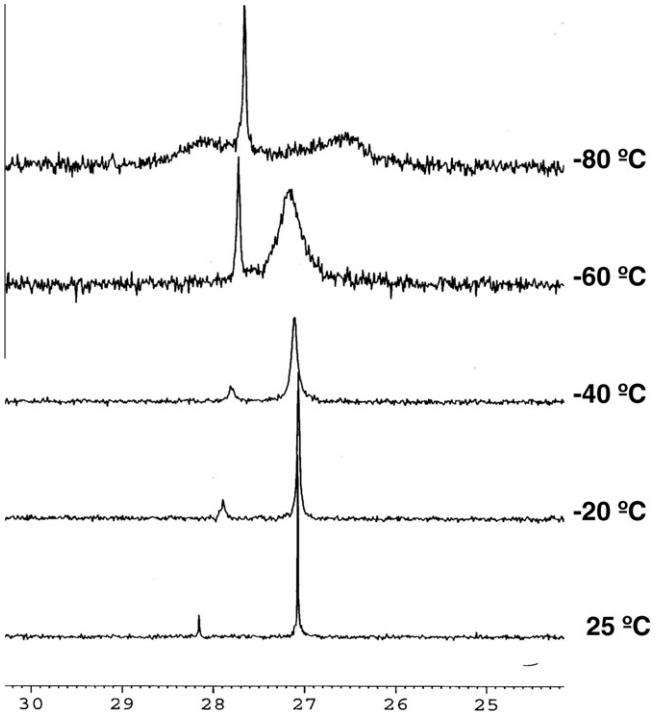


Fig. 4. Variable temperature ^{31}P NMR spectra of **10a** plus five equivalents of benzonitrile in CD_2Cl_2.

syn/anti isomerization (K_{eq2}) were determined for all wrap-around complexes. With these two strongly coordinating nitriles, acetonitrile and benzonitrile, wrap-around complexes bearing electron-withdrawing groups on the chelating olefinic moieties (**8a**–**8c**, **9a**, **11a**) are completely opened after the addition of ⩽2 equivalents of nitrile, whereas wrap-around complexes bearing electron-donating groups (**10a**–**10c**) exhibit a smaller K_{eq1} of 3 M^{-1}. The weakly coordinating 3,5-bis(trifluoromethyl)benzonitrile allows comparison of the equilibrium constants of all wrap-around complexes (Scheme 7 and Table 1). A larger equilibrium constant (K_{eq1}) signifies a greater preference for the open complex **B**, with the η^2-olefin being displaced by nitrile. Therefore, a large K_{eq1} is indicative of a more weakly bound η^2-olefin. Likewise, a smaller K_{eq1} indicates a more strongly bound olefin.

The binding affinity of the olefin was studied as a function of substituent X, the phosphine ligand, and the counteranion. It was found that electron-withdrawing groups (X = CO_2Me, Cl, entries 1–5) weaken the binding affinity of the η^2-wrap-around olefin, relative to the unsubstituted (X = H) systems (entries 6 and 7). Varying the phosphine ligand from PPh_3 to $P(NC_4H_4)_3$ also slightly influences the binding affinity of the olefin. Complex **8c** (entry 5) incorporates $P(NC_4H_4)_3$, which is a better π-acceptor that PPh_3, and shows a more weakly coordinated alkene arm relative to the analogous PPh_3 complex (entry 3). A small counterion effect was observed, with the more coordinating counterion, SbF_6^-, exhibiting a slightly larger equilibrium constant, K_{eq1}, than that of $B(Ar_F)_4^-$ (compare entries 3 and 4).

Table 1
Equilibrium constants determined by titration of wrap-around complexes with 3,5-bis(trifluoromethyl)benzonitrile.

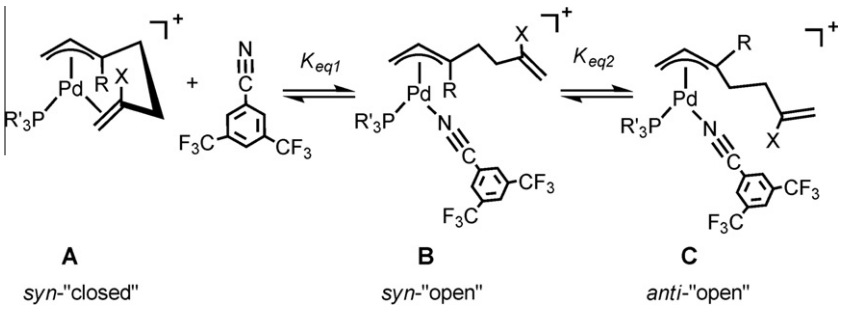
Entry	Wrap-around complex	K_{eq1} (M^{-1})[a]	K_{eq2}[a]
1	**9a**	230	<0.05
2	**11a**	180	0.5
3	**8a**	120	0.4
4	**8b**	100	0.6
5	**8c**	150	0.5
6	**10a**	<3	N/A
7	**10b**	<3	N/A

[a] Equilibrium constants were calculated at 25 °C.

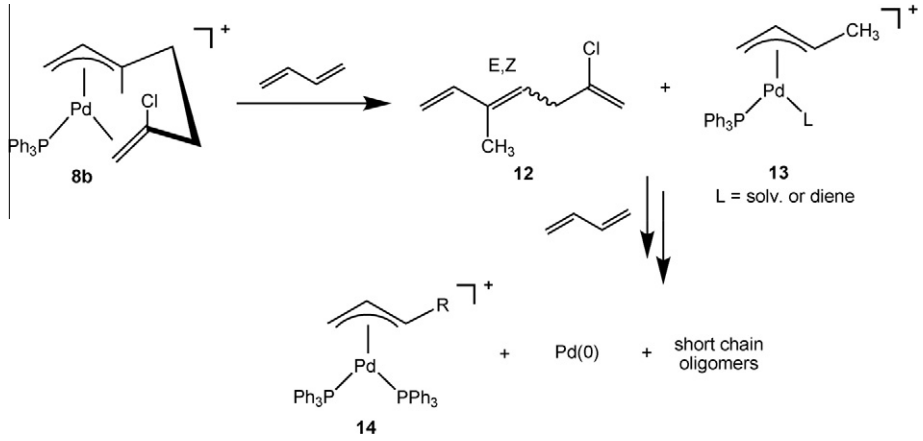
Once the wrap-around is in the open form, **B**, σ–π isomerization yields the mixture of the *syn* and *anti* open chain products, **B** and **C**, respectively. The ratio of *syn* and *anti* isomers is nearly unaffected by the substituents on the olefin arm, the type of phosphine, or the counterion. The *syn/anti* equilibrium (K_{eq2}) for all of the wrap-around complexes is essentially the same (ca. 0.5) and slightly favors the less sterically hindered *syn* isomer, with two exceptions. Wrap-around complex **9a** favors the *syn* species exclusively at room temperature and no isomerization is observed. This is attributed to the absence of a methyl group in the three position of the allyl unit and the high steric preference of a substituent for the *syn* position relative to the *anti* position. Additionally, the η^2-olefin arm in wrap-around complexes **10a** and **10b** were never displaced by excess bis(trifluoromethyl)benzonitrile as the olefin is very strongly bound to the metal and the nitrile is a weak ligand.

2.3. Attempted polymerization of isoprene and butadiene by wrap-around catalysts

Polymerization of 1,3-butadiene (BD) and isoprene (IP) was attempted using wrap-around complexes **8a**–**8c**, **10a**, **10c**, and **11a** as initiators in methylene chloride at room temperature and 50 °C for 20 h. Unfortunately, these reactions proceeded with very low conversions (2–12%) and produce only short chain oligomers, suggesting that the rate of chain transfer is likely comparable to or faster than the rate of propagation. Initial ^1H NMR spectroscopic investigations of the reactivity of wrap-around complexes with BD and IP at 25 °C showed decomposition of the catalyst via disproportionation to form a catalytically inactive bisphosphine species and palladium black upon monitoring after 20 h. As such, a closer examination of the reactivity with 1,3-dienes and the mechanism of chain transfer was undertaken by low temperature NMR spectoscopy.



Scheme 7. Wrap-around equilibrium with 3,5-bis(trifluoromethyl)benzonitrile.



Scheme 8. Chain transfer and trapping of the new Pd(II) complex.

2.4. Chain transfer with wrap-around catalysts

Addition of butadiene to **8a** or **8b** in an *in situ* NMR experiment resulted in chain transfer and formation of the triene **12** and trapping of one equivalent of BD to form a new crotyl π-allyl palladium(II) complex **13** at temperatures above −55 °C (Scheme 8). The crotyl complex **13** could not be isolated due to the labile nature of the solvent or diene in the fourth coordination site. However, trapping with triphenylphosphine yielded the bisphosphine complex **14**, which has been independently synthesized to confirm the ^{1}H and ^{31}P NMR spectral assignments of the *in situ* generated species. The organic product was isolated by vacuum removal of CD_2Cl_2 at −30 °C, extraction of the nonpolar triene product from the residue by cyclohexane-d_{12}, and then characterized by NMR spectroscopy and mass spectrometry (see Section 4 for details).

The chain transfer organic product, **12**, exists as a mixture of E and Z isomers in a 2:1 ratio, respectively. Two characteristic allylic peaks for each isomer resonate in the ^{1}H NMR spectrum at δ 6.65 and 5.48 for the E isomer, and at δ 6.33 and 5.39 for the Z isomer. Additionally, each isomer has a distinct resonance for the methyl group, appearing at δ 1.72 and 1.83 for the E and Z isomers, respectively.

The kinetics of this chain transfer process were studied by ^{1}H NMR spectroscopy. In a typical experiment, a screw-cap NMR tube was charged with a methylene chloride-d_2 solution of **8b** and 5–20 equivalents of BD at −45 °C and monitored for 35 min. To determine the order in [BD], the observed rate constants for chain transfer were measured over several diene concentrations while holding the initial concentration of **8b** constant. The results of these experiments are shown in Fig. 5 and summarized in Table 2. A first-order

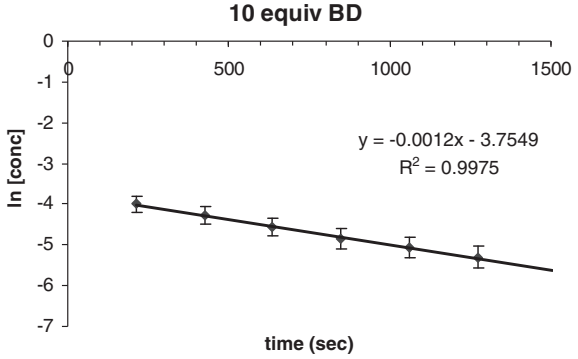


Fig. 5. Kinetic plot of the disappearance of the wrap-around complex **8b** over time upon addition of 10 equivalents of 1,3-butadiene.

Table 2
Influence of [BD] on the rate of chain transfer for complex **8b**.

Equivalents BD	Temperature (°C)	Rate (s^{-1})
5	−45	0.8×10^{-3}
10	−45	1.2×10^{-3}
20	−45	2.9×10^{-3}

rate dependence on [BD] is observed for the chain transfer event. This is in contrast to previous findings for π-allyl Ni(II) systems, where the rate of chain transfer in butadiene polymerization reactions is independent of the concentration of diene [4].

These differences suggest that, while the π-allyl Ni(II) systems are highly active for BD and IP polymerization, the π-allyl Pd(II) systems suffer from a fast rate of chain transfer relative to the rate of polymerization, resulting in dimerization or oligomerization of BD and IP for the analogous Pd(II) systems.

3. Summary

Syntheses and characterizations of several easily-tunable wrap-around complexes **8a**–**8c**, **9a**, **10a**–**10c**, and **11a** have been described (see Scheme 5). Single crystal X-ray structural determinations of **8a** and **8a** reveal 16-electron π-allyl complexes with a chelating olefin arm. The η^2-chelating olefin arm can be displaced by nitriles of varying strengths via titration of a solution of wrap-around complex with various equivalents of nitriles. These titration experiments lend insight into the relative binding affinity of the chelating olefin arm. Electron-withdrawing substituents on the olefin (X = –COOMe, –Cl) allowed for facile displacement of the η^2-olefin by nitrile, whereas an unsubstituted vinyl group was more strongly bound to the palladium center and could not be effectively displaced by nitrile. Counterion and phosphine substituent effects were relatively minor and had very little influence on the binding affinity of the olefin arm. Attempted catalytic polymerization of isoprene and 1,3-butadiene by wrap-around complexes yielded short chain oligomers with very poor conversions and catalyst decomposition. Low temperature NMR analysis shows wrap-around **8b** reacts with butadiene at −55 °C in what corresponds to a chain transfer process to yield a triene and a methallyl complex. This process was examined kinetically and found to be first-order in [BD], in contrast to the zero-order butadiene dependence of the chain transfer process found for polymerization of butadiene by ligand-free (π-allyl)Ni(II) complexes. The fast rate of chain transfer for these Pd(II) systems adequately explains the lack of polymerization activity for BD and IP.

4. Experimental

4.1. General considerations

All reactions, unless otherwise stated, were conducted under an atmosphere of dry, oxygen free argon using standard high-vacuum, Schlenk, or drybox techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. Palladium catalysts were stored in an MBraun glovebox at −35 °C to prevent thermal decomposition. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker DRX 500 MHz or a Bruker DRX 400 MHz spectrometer. Chemical shifts were referenced relative to residual $CHCl_3$ (δ 7.24 for ^{1}H) and $CH(D)Cl_2$ (δ 5.32 for ^{1}H), CD_2Cl_2(δ 53.8 for ^{13}C), $CDCl_3$ (δ 77.0 for ^{13}C). Assignments were supported by ^{1}H–^{13}C HMQC, ^{1}H–^{1}H COSY, and NOESY experiments. Elemental analyses were carried out by Atlantic Microlab, Inc., of Norcross, GA. GPC analyses were performed in HPLC grade tetrahydrofuran at 25 °C using a Waters Alliance HPLC equipped with Waters Styragel HR2, HR4, and HR5 columns and a Waters 410 refractive index detector. Molecular weights are reported relative to polystyrene standards. The crystallographic information for **1a** and **2a** is reported in Appendix A. The data was obtained on a Bruker SMART APEX-2 X-ray diffractometer a −173 °C using Mo Kα radiation.

4.2. Materials

All solvents were deoxygenated and dried by passage over columns of activated alumina [16,17]. Isoprene and 1,3-butadiene were purchased from Aldrich and purified by vacuum transfer through 4 Å molecular sieves and stored over 4 Å molecular sieves at −35 °C under argon. Methylene chloride-d_2 and chloroform-d were purchased from Cambridge Isotope Laboratories and stored over 4 Å molecular sieves. $NaB(Ar_F)_4$ was purchased from Boulder Scientific. Allyl chloride, allyl bromide, $AgSbF_6$, $PdCl_2$, LiCl, and tripyrrolidinylphosphine were purchased from Aldrich and used as received. Tripyrrolylphosphine was prepared according to literature methods [18]. The π-allyl palladium halide dimers were synthesized according to literature procedures [11].

4.3. (Allyl)Pd(II) complex synthesis

4.3.1. Synthesis of [(IP-2-Cl-π-allyl)PdCl]$_2$

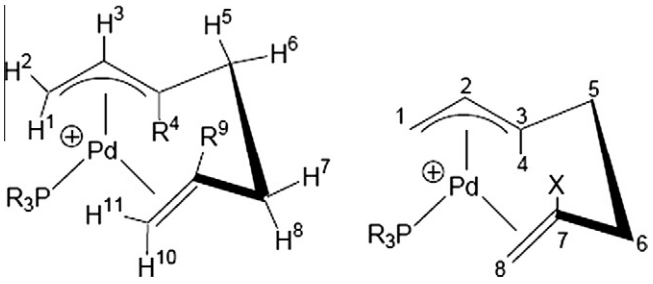
Under an argon atmosphere, [(2-Cl-π-allyl)PdCl]$_2$ (0.600 g, 1.38 mmol) and excess isoprene (6.3 mL, 69.0 mmol) were dissolved in dry methylene chloride (40 mL). The solution was allowed to stir for ca. 30 min at room temperature until one equivalent of diene had inserted into the palladium-allyl bond as determined by ^{1}H NMR analysis. The solvent was removed *in vacuo* to yield the dimer as a yellow oil. The product was washed with dry pentane (3 × 20 mL) to yield the product as an isolable powder. Yield: 0.702 g (89%).

4.3.2. General procedure for the synthesis of complexes 8a–**8c**

Under an argon atmosphere, [(IP-2-Cl-π-allyl)PdCl]$_2$ and two equivalents triphenylphosphine were dissolved in dry methylene chloride (20 mL) and the resulting yellow solution was stirred at room temperature for 5 min. A solution of two equivalents silver hexafluoroantimonate in 5 mL methylene chloride was then added via cannula at −78 °C and the mixture was stirred for an additional hour at this temperature before the solution was allowed to slowly warm to room temperature. The resulting solution was filtered through celite and the solvent evaporated *in vacuo*. The product was washed with 3 × 10 mL of dry pentane and dried under vacuum to yield a yellow powder.

4.4. General numbering scheme

4.4.1. [Pd(IP-2Cl)PPh$_3$][SbF$_6$] (**8a**)



The general procedure was employed using [(IP-2-Cl-π-allyl)PdCl]$_2$ (0.200 g, 0.460 mmol), triphenylphosphine (0.190 g, 0.74 mmol), and silver hexafluoroantimonate (0.250 g, 0.74 mmol). Yield: 0.365 g (64%). $^{1}H\{^{31}P\}$ NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.40–7.70 (m, 15H, PPh_3), 6.24 (dd, $^{3}J_{HHsyn}$ = 13 Hz, $^{3}J_{HHanti}$ = 7.6 Hz, 1H, H_3), 4.93 (s, 1H, H_{10}), 4.41 (s, 1H, H_{11}), 4.04 (dd, $^{3}J_{HH}$ = 16 Hz, $^{3}J_{HH}$ = 12 Hz, $^{3}J_{HH}$ = 4.0 Hz, 1H, H_8), 3.66–3.76 (m, 2H, H_6+H_2), 3.32–3.42 (m, 2H, H_1+H_7), 2.76 (m, 1H, H_5), 1.87 (s, 3H, R_4 = CH_3). $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 28.7. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C): δ 20.8 (d, $^{3}J_{CP}$ = 3.7 Hz, C_4), 45.2 (s, C_5), 49.3 (d, J = 5.0 Hz, C_6), 61.3 (s, C_1), 90.2 (s, C_8), 116.0 (d, J = 3.7 Hz, C_2), 130.3 (d, C_9), 129.9 (d, $^{3}J_{CP}$ = 10.8 Hz, PPh_3), 132.1 (d, $^{4}J_{CP}$ = 2.1 Hz, PPh_3), 133.8 (d, $^{2}J_{CP}$ = 13.1 Hz, PPh_3), 139.3 (d, $^{2}J_{CP}$ = 19.2 Hz, C_3), 145.2 (s, C_7). *Anal.* Calc. for $C_{26}H_{27}PClPdSbF_6$ (748.12): C, 41.74; H, 3.65. Found: C, 42.15; H, 3.67%.

4.4.2. [Pd(IP-2Cl)PPh$_3$][B(Ar$_F$)$_4$] (**8b**)

The general procedure was employed using [(IP-2-Cl-π-allyl)PdCl]$_2$ (0.200 g, 0.460 mmol), triphenylphosphine (0.190 g, 0.74 mmol), and $NaB(Ar_F)_4$ (0.620 g, 0.74 mmol). Yield: 0.698 g (72%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.4–7.6 (m, 15H, PPh_3), 6.18 (dd, $^{3}J_{HHsyn}$ = 13.2 Hz, $^{3}J_{HHanti}$ = 7.4 Hz, 1H, H_3), 1.79 (d, $^{4}J_{HP}$ = 5.2 Hz, 3H, R_4 = CH_3), 4.73 (s, 1H, H_{10}), 4.46 (d, $^{3}J_{HH}$ = 5.6 Hz, 1H, H_{11}), 3.86 (td, $^{3}J_{HH}$ = 4.0 Hz, $^{3}J_{HH}$ = 13.8 Hz, 1H, H_8), 3.70 (dd, 1H, H_2), 3.68 (m, 1H, H_7), 3.35 (dd, $^{2}J_{HH}$ = 2.4 Hz, $^{3}J_{HH}$ = 13.2 Hz, 1H, H_1), 3.34 (m, 1H, H_6), 2.73 (m, 1H, H_5). $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 26.9. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ 162.0 (q, $^{1}J_{CB}$ = 49.8 Hz, $B(Ar_F)_4$ C_{ipso}), 145.2 (s, C_7), 138.2 (d, C_3), 135.2 (s, $B(Ar_F)_4$ C_o), 133.8 (d, $^{2}J_{CP}$ = 13.0 Hz, Ph_3), 132.3 (d, $^{4}J_{CP}$ = 2.4 Hz, Ph_3), 130.1 (d, C_9), 129.9 (d, $^{3}J_{CP}$ = 10.8 Hz, Ph_3), 129.2 (q, $^{2}J_{CF}$ = 31.5 Hz, $B(Ar_F)_4$ C_m), 128.3, 126.1, 123.9, 121.8 (q, $^{1}J_{CF}$ = 272.9 Hz, $B(Ar_F)_4$ CF_3), 117.9 ($B(Ar_F)_4$ C_p), 116.1 (s, C_2), 90.3 (s, C_8), 61.2 (s, C_1), 49.2 (s, C_6), 45.0 (s, C_5), 20.8 (s, C_4). *Anal.* Calc. for $C_{58}H_{39}PClPdB(Ar_F)_4$ (1375.62): C, 50.64; H, 2.86. Found: C, 50.61; H, 2.89%.

4.4.3. [Pd(IP-2Cl)P(NC$_4$H$_4$)$_3$][SbF$_6$] (**8c**)

The general procedure was employed using [(IP-2-Cl-π-allyl)PdCl]$_2$ (0.150 g, 0.26 mmol), tripyrrolylphosphine (0.120 g, 0.53 mmol), and silver hexafluoroantimonate (0.180 g, 0.53 mmol). Yield: 0.295 g (78%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 6.83 (s, 6H, $P(NC_4H_4)_3$), 6.54 (s, 4H, $P(NC_4H_4)_3$), 6.31 (m, 1H, H_3), 1.92 (d, $^{4}J_{HP}$ = 7.2 Hz, 3H, R_4 = CH_3), 5.11 (s, 1H, H_{10}), 4.43 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H, H_{11}), 3.96 (td, $^{3}J_{HH}$ = 12.8 Hz, $^{3}J_{HH}$ = 3.2 Hz, 1H, H_8), 4.23 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{2}J_{HH}$ = 2.4 Hz, 1H, H_2), 3.68 (m, 1H, H_7), 3.67 (d, $^{3}J_{HH}$ = 12.8 Hz, 1H, H_1), 3.28 (m, 1H, H_6), 2.78 (m, 1H, H_5), 1.96 (s, $^{3}J_{HP}$ = 7.2 Hz, 3H, R_4 = CH_3). $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 95.2. *Anal.* Calc. for $C_{20}H_{24}PClN_3PdSbF_6$ (714.79): C, 33.59; H, 3.39. Found: C, 33.66; H, 3.36%.

4.4.4. [Pd(BD-2Cl)PPh_3][SbF_6] (**9a**)

The general procedure was employed using [(2-Cl-π-allyl) PdCl]$_2$ (2.63 mmol) and excess butadiene (6.22 g, 0.115 mol) to form the isolable butadiene inserted palladium chloride dimer. For the second step, [Pd(BD-2Cl)Cl]$_2$ (0.100 g, 0.18 mmol), triphenylphosphine (0.097 g, 0.37 mmol) and $AgSbF_6$ (0.127 g, 0.37 mmol) were used. Yield: 0.214 g (79%). $^1H\{^{31}P\}$ NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.4–7.6 (m, 15H, PPh_3), 6.34 (dt, $^3J_{HHsyn}$ = 12 Hz, $^3J_{HHanti}$ = 6 Hz, 1H, H_3), 6.04 (dt, $^3J_{HH}$ = 12 Hz, $^3J_{HH}$ = 4.0 Hz, 1H, R_4 = H), 5.11 (s, 1H, H_{10}), 4.48 (s, 1H, H_{11}), 4.00 (td, $^3J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 4.4 Hz, 1H, H_8), 3.73 (dd, $^3J_{HH}$ = 7.0 Hz, $^2J_{HH}$ = 2.0 Hz, 1H, H_2), 3.51 (m, 1H, H_7), 3.45 (d, $^3J_{HH}$ = 12.8 Hz, 1H, H_1), 3.26 (m, 1H, H_6), 2.86 (m, 1H, H_5). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 26.4. *Anal.* Calc. for $C_{25}H_{24}PClPdSbF_6$ (733.08): C, 40.96; H, 3.31. Found: C, 41.01; H, 3.53%.

4.4.5. General procedure for the synthesis of complexes 10a–**10c** and **11a**

Under an argon atmosphere, [(π-allyl)PdBr]$_2$ (0.200 g, 0.40 mmol) was dissolved in dry methylene chloride (20 mL) and then an excess of isoprene (2.3 mL, 23.0 mmol) was added. The solution was allowed to stir for 1–2 days until one equivalent of diene had inserted into the palladium-allyl bond as monitored by ^1H NMR spectroscopy. The solvent was removed *in vacuo* to yield the dimer as a yellow oil which was not isolated but was carried on directly to the next step. The dimer and triphenylphosphine (0.209 g, 0.80 mmol) were dissolved in dry methylene chloride (20 mL) and the resulting yellow solution was stirred at room temperature for 5 min. Next, two equivalents silver hexafluoroantimonate or $NaB(Ar_F)_4$ were added at −78 °C and the mixture was stirred for an additional hour before the solution was allowed to slowly warm to room temperature. The resulting solution was filtered through celite and the solvent evaporated *in vacuo*. The product was washed with 3 × 10 mL of dry pentane and dried under vacuum to yield a yellow powder.

4.4.6. [Pd(IP-2H)PPh_3][SbF_6] (**10a**)

The general procedure was employed using $AgSbF_6$ (0.274 g, 0.80 mmol). Yield: 0.623 g (78%). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.30–7.70 (m, 15H, PPh_3), 6.24 (dd, $^3J_{HHsyn}$ = 12.8 Hz, $^3J_{HHanti}$ = 7.4 Hz, 1H, H_3), 6.48 (m, 1H, R_9 = H), 4.52 (d, $^3J_{HH}$ = 16.8, 1H, H_{10}), 4.34 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.7 Hz, 1H, H_{11}), 3.59 (d, $^3J_{HH}$ = 7.4, 1H, H_2), 3.30 (d, $^3J_{HH}$ = 12.8 Hz, 1H, H_1), 3.26–3.39 (m, 2H, H_7+H_6), 3.15 (m, 1H, H_8), 2.71 (pt, 1H, H_5), 1.73 (d, $^3J_{HP}$ = 4.4 Hz, 3H, R_4 = CH_3). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 26.6. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 25 °C): δ 20.6 (s, C_4), 42.1 (d, J = 4.8 Hz, C_6), 46.2 (s, C_5), 61.1 (s, C_1), 92.3 (s, C_8), 116.4 (d, $^2J_{CP}$ = 3.7 Hz, C_2), 129.8 (d, $^3J_{CP}$ = 10.6 Hz, PPh_3), 130.6 (d, $^1J_{CP}$ = 43.8 Hz, PPh_3), 114.0 (d, $^4J_{CP}$ = 2.4 Hz, PPh_3), 132.3 (s, C_7), 133.7 (d, $^2J_{CP}$ = 13.0 Hz, PPh_3), 140.1 (d, $^2J_{CP}$ = 19.9 Hz, C_3). *Anal.* Calc. for $C_{26}H_{28}PPdSbF_6$ (712.65): C, 43.75; H, 3.96. Found: C, 43.56; H, 4.00%.

4.4.7. [Pd(IP-2H)PPh_3][$B(Ar_F)_4$] (**10b**)

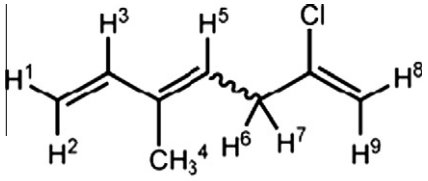
The general procedure was employed using $NaB(Ar_F)_4$ (0.706 g, 0.80 mmol). Yield: 0.936 g (64%). ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.30–7.70 (m, 15H, PPh_3), 7.63 and 7.52 (s and s, 12H, $B(Ar_F)_4$), 6.11 (dd, $^3J_{HHsyn}$ = 14.8 Hz, $^3J_{HHanti}$ = 7.4 Hz, 1H, H_3), 6.36 (m, 1H, R_9 = H), 4.49 (d, $^3J_{HH}$ = 16.4 Hz, 1H, H_{10}), 4.35 (dd, $^3J_{HH}$ = 7.6 Hz, 1H, H_{11}), 3.59 (dd, $^2J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 7.4 Hz, 1H, H_2), 3.3 (m, 3H, H_8+H_7+H_6), 3.11 (d, $^3J_{HH}$ = 14.8 Hz, 1H, H_1), 2.64 (pt, 1H, H_5), 1.69 (d, $^3J_{HP}$ = 4.4 Hz, 3H, R_4 = CH_3). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 26.9. *Anal.* Calc. for $C_{58}H_{40}PPdB(Ar_F)_4$ (1339.75): C, 51.94; H, 3.01. Found: C, 51.35; H, 2.89%.

4.4.8. [Pd(IP-2H)$P(NC_4H_4)_3$][SbF_6] (**10c**)

The general procedure was employed using $AgSbF_6$ (0.274 g, 0.797 mmol). Yield: 0.360 g (66%). ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 6.83 (s, 6H, $P(NC_4H_4)_3$), 6.54 (s, 4H, $P(NC_4H_4)_3$), 6.71 (m, 1H, R^9 = H), 6.48 (m, 1H, R_9 = H), 6.40 (dd, $^3J_{HHsyn}$ = 16.8 Hz, $^3J_{HHanti}$ = 7.5 Hz, 1H, H_3), 4.71 (d, $^3J_{HH}$ = 16.8, 1H, H_{10}), 4.44 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 8.1 Hz, 1H, H_{11}), 4.12 (d, $^3J_{HH}$ = 7.5, 1H, H_2), 3.53–3.40 (m, peak overlap, 3H, H_1+ H_7+H_8), 3.20 (m, 1H, H_6), 2.74 (pt, 1H, H_5), 1.82 (d, $^3J_{HP}$ = 7.2 Hz, 3H, R_4 = CH_3). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 95.7.

4.4.9. [Pd(IP-2COOMe)(PPh_3)][SbF_6] (**11a**)

The general procedure was employed using [(2-COOMe-π-allyl) PdCl]$_2$ (0.200 g, 0.83 mmol), triphenylphosphine (0.436 g, 1.66 mmol) and $AgSbF_6$ (0.571 g, 1.66 mmol). Yield: 0.795 g (62%). $^1H\{^{31}P\}$ NMR (400 MHz, CD_2Cl_2, −40 °C): δ 7.30–7.70 (m, 15H, PPh_3), 6.28 (dd, $^3J_{HHsyn}$ = 13 Hz, $^3J_{HHanti}$ = 7.6 Hz, 1H, H_3), 5.11 (s, 1H, H_{10}), 4.85 (s, 1H, H_{11}), 3.84 (d, $^3J_{HH}$ = 7.4 Hz, 1H, H_2), 3.66 (m, 1H, H_8), 3.57 (s, 3H, R_9 = $COOCH_3$), 3.40–3.55 (m, 2H, H_7+H_6), 3.12 (d, $^3J_{HH}$ = 12.8 Hz, 1H, H_1), 2.61 (pt, $^3J_{HH}$ = 11 Hz, 1H, H_5), 1.78 (s, 3H, R_4 = CH_3). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 27.9. *Anal.* Calc. for $C_{28}H_{30}O_2PPdSbF_6{\cdot}2\ CH_2Cl_2$ (941.58): C, 38.26; H, 3.65. Found: C, 38.20; H, 3.68%



E,Z

12

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4.4.10. Characterization of the organic chain transfer product 12

Addition of 1,3-butadiene to **8a** or **8b** resulted in chain transfer and formation of the organic product and a new palladium(II) allyl complex (Scheme 8). The organic product was isolated by vacuum removal of the solvent at −30 °C, dissolved in cyclohexane-d_{12}, and characterized by NMR and ESI+ mass spectrometry. The ratio of E–Z isomers was 2:1. Characterization of E isomer: ^1H NMR (500 MHz, C_6D_{12}, 25 °C): δ 6.65 (dd, $^3J_{H3-H1}$ = 10.5 Hz, $^3J_{H3-H2}$ = 17.5 Hz, 1H, H^3), 5.48 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H^5), 5.10 (d, $^3J_{HH}$ = 17.5 Hz, 1H, H^2), 5.08 (s, 1H, H^8), 5.03 (s, 1H, H^9), 4.94 (d, $^3J_{HH}$ = 10.5 Hz, 1H, H^1), 3.11 (dd, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 9.5 Hz, 1H, H^6+H^7), 1.72 (s, 3H, $CH_3{}^4$). Characterization of Z isomer: ^1H NMR (500 MHz, C_6D_{12}, 25 °C): δ 6.33 (dd, $^3J_{H3-H1}$ = 10.5 Hz, $^3J_{H3-H2}$ = 17.5 Hz, 1H, H_3), 5.39 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, 1H, H^5), 5.21 (d, $^3J_{HH}$ = 17.5 Hz, 1H, H^2), 5.08 (s, 1H, H^8), 5.03 (s, 1H, H^9), 5.00 (d, $^3J_{HH}$ = 10.5 Hz, 1H, H^1), 3.11 (dd, $^3J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 9.5 Hz, 1H, H^6+H^7), 1.83 (s, 3H, $CH_3{}^4$). ESI-MS (methanol:cyclohexane (50:1), +ion scan, *m/z*): 142.1 Da (expected: 142.055 Da).

4.4.11. In situ generated methallyl phosphine complex **13**

A screw-cap NMR tube was charged with **8b** (0.028 g, 0.021 mmol) dissolved in 500 μL CD_2Cl_2. Two equivalents of 1,3-butadiene were then added at low temperature. The chain transfer reaction was monitored via ^1H NMR for 50 min, at which point all of the original starting wrap-around complex **8b** had undergone chain transfer and insertion of one equivalent of 1,3-butadiene formed the (π-methallyl)Pd(triphenylphosphine)(solvent or diene) complex **13**. ^1H NMR (400 MHz, CD_2Cl_2, −45 °C): δ 7.50–7.30 (m, 15H, PPh_3), 5.72 (m, H_c, 1H), 4.42 (m, H^1, 1H), 3.97 (d, $^3J_{HH}$ = 4.8 Hz,

H_{syn}, 1H), 2.83 (d, $^3J_{HH}$ = 12.4 Hz, H_{anti}, 1H), 1.98 (bs, C$\underline{H}_3$, 3H). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, −45 °C): δ 27.7 (bs, $\underline{P}Ph_3$).

*4.4.12. In situ generated methallyl bisphosphine complex **14***

A screw-cap NMR tube was charged with **8b** (0.028 g, 0.021 mmol) dissolved in 500 μL CD_2Cl_2. Two equivalents of 1,3-butadiene were added at low temperature, and the chain transfer reaction was monitored at −20 °C via ^1H NMR for 50 min, at which point all of the original starting wrap-around complex **8b** had undergone chain transfer and formed the (π-methallyl)Pd(triphenylphosphine)(solvent or diene) complex **13**. Then, one equivalent of triphenylphosphine (5.5 mg, 0.021 mmol) was added via syringe to the solution to form the (π-methallyl)Pd$(PPh_3)_2$ complex **14**. Only the major isomer was observed. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.50–7.10 (m, 30H, PPh_3), 5.63 (m, H_c, 1H), 4.26 (m, H^1, 1H), 3.53 (dd, $^3J_{HH}$ = 6.4 Hz, J_{HP} = 6.4 Hz, H_{syn}, 1H), 3.21 (dd, $^3J_{HH}$ = 10.4 Hz, J_{HP} = 10.4 Hz, H_{anti}, 1H), 1.05 (m, C$\underline{H}_3$, 3H). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 26.4 (d, $^2J_{PP}$ = 40.7 Hz, PPh$_3$), 25.5 (d, $^2J_{PP}$ = 40.7 Hz, $\underline{P}Ph_3$).

*4.4.13. Synthesis of methallyl bisphosphine complex **14***

In a Schlenk tube under an argon atmosphere, [(π-methallyl)PdCl]$_2$ (0.100 g, 0.254 mmol) and four equivalents of triphenylphosphine (0.266 g, 1.02 mmol) were dissolved in dry methylene chloride (20 mL) and then cooled in a dry ice/isopropyl alcohol bath to −78 °C. A solution of two equivalents silver hexafluoroantimonate (0.150 g, 0.440 mmol) in 5 mL methylene chloride was then added dropwise at −78 °C and the mixture was stirred for ca. 30 min at low temperature before the solution was allowed to warm slowly to room temperature. The resulting solution was cannula filtered and the solvent evaporated *in vacuo*. The product was washed with 3 × 10 mL of pentane and dried under vacuum to yield the product as a yellow powder. Yield: 0.375 g (80%). The ratio of major (*syn*) to minor (*anti*) product was 12:1. Characterization of major (*syn*) isomer: ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.50–7.10 (m, 30H, PPh_3), 5.63 (m, H_c, 1H), 4.26 (m, H^1, 1H), 3.53 (dd, $^3J_{HH}$ = 6.4 Hz, J_{HP} = 6.4 Hz, H_{syn}, 1H), 3.21 (dd, $^3J_{HH}$ = 10.4 Hz, J_{HP} = 10.4 Hz, H_{anti}, 1H), 1.05 (m, C$\underline{H}_3$, 3H). Characterization of minor (*anti*) isomer: ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.50–7.10 (m, 30H, PPh_3), 5.63 (m, H_c, 1H, overlap with major isomer), 4.79 (m, H^1, 1H), 4.21 (dd, H_{syn}, 1H), 3.21 (dd, H_{anti}, 1H, overlap with major isomer), 1.05 (m, C$\underline{H}_3$, 3H, overlap with major isomer). $^{31}P\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 25 °C): δ 26.4 (d, $^2J_{PP}$ = 40.7 Hz, PPh$_3$, major isomer), 25.5 (d, $^2J_{PP}$ = 40.7 Hz, $\underline{P}Ph_3$, major isomer), 25.1 (d, $^2J_{PP}$ = 39.6 Hz, $\underline{P}Ph_3$, minor isomer), 24.2 (d, $^2J_{PP}$ = 39.6 Hz, PPh$_3$, minor isomer).

4.4.14. General procedure for titration experiments

A screw-cap NMR tube was charged with ca. 10.0 mg of the wrap-around complexes **8a**–**8c**, **9a**, **10a**–**10c**, and **11a** dissolved in 500 μL of deuterated methylene chloride under inert atmosphere. NMR spectra were taken after 0, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, and 40 equivalents of nitrile were added via a 10 μL gas tight syringe at room temperature; a typical series of spectra are shown in Section 2. Chemical shifts for H_3, R_4 = Me, and the vinylic protons, H_{10} and H_{11}, were monitored and recorded. The first equilibrium (K_1, as described by text) was fast on the NMR time scale and thus the resonance monitored (typically the allylic peak, H_3) was an average of that for **A and B.** Once the chemical shifts of the fully closed complex (**A**), the fully open complex (**B**), and the observed signal averaged peak (closed ↔ open) were recorded, Eq. (2) was employed to determine the fraction of the closed (**A**) and open (**B** + **C**) complexes. The concentration of closed and open was then determined by multiplying the respective fraction by the total palladium(II) concentration, calculated from the initial moles of palladium(II) wrap-around complex added over the total solution volume and taking into account the added nitrile. From the total open concentration [**B** + **C**], the concentrations of **B** and **C** were calculated from their respective integrals. With all these known values, the equilibria constants K_{eq1} and K_{eq2} were determined.

$$\delta_{obs} = (1.00 - F_{open})\mathbf{A}^{closed} + (F_{open})\mathbf{B}^{open}$$

$$F_{open} = \left[\delta_{obs} - \mathbf{A}^{closed}\right] / \left[\mathbf{B}^{open} - \mathbf{A}^{closed}\right] \quad (2)$$

$\mathbf{A}^{closed} = \delta$ for starting complex or δ when completely closed (olefin is η^2 bound to form the wrap-around); $\mathbf{B}^{open} = \delta$ when the complex is completely "open"; F_{open} = fraction of complex (out of 1.00 total) that is "open".

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Appendix A. Supplementary material

CCDC 804318 and 804319 contains the supplementary crystallographic data for structures **8a** and **9a**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.046.

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