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Dinuclear [{(π-C_3H_5)M(PR_3)}$_2$(μ-X)]Y Complexes of Nickel and Palladium[†]

Davide Alberti, Richard Goddard, and Klaus-Richard Pörschke*

Max-Planck-Institut für Kohlenforschung, D-45466 Mülheim an der Ruhr, Germany

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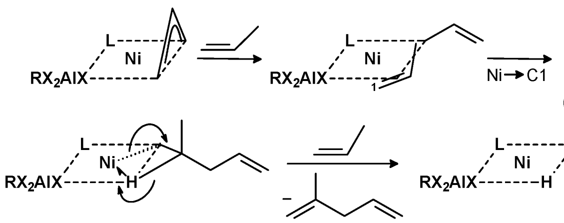
The double halide-bridged π-allyl complexes {(η^3-C_3H_5)M(μ-X)}$_2$ (M = Ni, Pd; X = Cl, Br) resist halide abstraction by thallium salts of weakly coordinating anions Y = PF_6, B(C_6F_5)$_4$, and B{$C_6H_3(CF_3)_2$}$_4$ in noncoordinating CH_2Cl_2. In the presence of a bulky phosphine (P^iPr_3, P^tBu_3) or when 2 equiv of (η^3-C_3H_5)M(PR_3)X is reacted with TlY, one of the halide ions is replaced to afford the ionic dinuclear, single halide-bridged complexes [{(η^3-C_3H_5)M(PR_3)}$_2$(μ-X)]Y (M = Ni, X = Br (**6**, **7**); M = Pd, X = Cl (**8**, **9**) and Br (**10**, **11**)), which do not react with further TlY. The corresponding complexes with Y = Al{OC(CF_3)$_3$}$_4$ have also been prepared. In addition, it has been found that the dinuclear palladium complexes, but not the nickel derivatives, are also stable for Y = OTf. According to NMR the complexes represent a mixture of diastereomers in solution. For [{(η^3-C_3H_5)Ni(P^iPr_3)}$_2$(μ-Br)][Al{OC(CF_3)$_3$}$_4$] (**6c**) and [{(η^3-C_3H_5)Pd(P^tBu_3)}$_2$(μ-Br)][B(C_6F_5)$_4$] (**11b**) the crystal structures have been determined. The reaction of (η^3-C_3H_5)M(PMe_3)X with TlY affords a mixture of [(η^3-C_3H_5)M(PMe_3)$_2$]Y (described for M = Ni, Y = PF_6 (**12**) and M = Pd, Y = PF_6 (**13**)) and the starting phosphine-free {(η^3-C_3H_5)M(μ-X)}$_2$.

Introduction

(η^3-allyl)Ni-halide complexes are important *precursor* complexes for homogeneous catalysts. The halide bridges in the pristine dimeric {(η^3-C_3H_5)Ni(μ-X)}$_2$ (X = Cl, Br, I; **1**) are certainly relatively strong and resist, for instance, cleavage by alkenes such as ethene and 1,5-cyclooctadiene (cod) or by CO, and accordingly the catalytic activity of {(η^3-C_3H_5)Ni(μ-X)}$_2$ for olefin oligomerization is low. However, the activity increases considerably by addition of Lewis acids and phosphines.[1] Indeed, reaction of **1** with 1 equiv of phosphine per nickel results in cleavage of both halide bridges to yield mononuclear complexes (η^3-C_3H_5)Ni(PR_3)X (**2**), which are more active than the pristine **1**. Addition of aluminum halides R'_nAlX_{3-n} (n = 0−2) to **1** also cleaves the Ni−X−Ni bridges, but gives red oily, polar adducts (η^3-C_3H_5)Ni(R'_nAlX_{4-n}) (R′ = alkyl, X; **3**), which have a catalytic activity toward ethylene and propylene several orders higher than that of the starting **1**. The structure of **3** is likely to be square-planar with the (η^3-C_3H_5)Ni moiety chelated by R'_nAlX_{4-n}, i.e., (η^3-C_3H_5)Ni(μ-X)$_2$AlR'_nX_{2-n}.[1e] An initially invoked ionic structure [(η^3-C_3H_5)Ni][AlR'_nX_{4-n}][1a,b] has since been discarded.

Reactions of either **2** with an aluminum halide or **3** with a phosphine result in isolable adducts (η^3-C_3H_5)Ni(PR_3)(μ-X)AlR'_nX_{3-n} (**4**), of which the derivative (η^3-C_3H_5)Ni(PCy_3)(μ-Cl)AlMeCl_2 (**4a**) has been characterized by X-ray structure analysis.[2] Complexes of this type are most active for the catalytic dimerization of propene, and highest activity paired with highest selectivity has been observed for a $P^tBu^iPr_2$ modified catalyst. The halide bridges in **3** and **4** are weaker than in **1**, and they are cleaved with cod and CO, as well as PR_3, to give rise to inactive ionic complexes [(η^3-C_3H_5)NiL_2][R'_nAlX_{4-n}] (**5**) with tightly coordinated ligands L (Scheme 1).[1]

It is important to emphasize that the complexes **2**−**4** are only precursor complexes of the true catalytically active species, which has actually been identified as a nickel hydride. This is formed in a stoichiometric reaction by π−σ-allyl isomerization and insertion of propyne into the Ni−C bond, followed by β-H abstraction (eq 1).



(1)

Other important reactions involving the (η^3-allyl)M(PR_3)X unit (M = Ni, Pd) are the (η^3-allyl)Ni(P^iPr_3)X/AgY (Y = BF_4, ClO_4, CF_3SO_3) catalyzed cyclization of 1,5- and 1,6-dienes[3] and the (η^3-C_3H_5)Ni(PMe_3)Cl/$AgBF_4$-

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[†] Dedicated to Günther Wilke on the occasion of his 80th birthday (February 23, 2005), in recognition of his seminal studies in metal-allyl chemistry.

[1] (a) Birkenstock, U.; Bönnemann, H.; Bogdanovic, B.; Walter, D.; Wilke, G. *Adv. Chem. Ser.* **1968**, *70*, 250. (b) Bogdanovic, B.; Wilke, G. *Brennstoff-Chemie* **1968**, *49*, 323. (c) Bogdanovic, B.; Henc, B.; Karmann, H.-G.; Nüssel, H.-G.; Walter, D.; Wilke, G. *Ind. Eng. Chem.* **1970**, *62*, Nr. 12, p 34. (d) Bogdanovic, B.; Henc, B.; Lösler, A.; Meister, B.; Pauling, H.; Wilke, G. *Angew. Chem.* **1973**, *85*, 1013; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 954. (e) Bogdanovic, B. *Adv. Organomet. Chem.* **1979**, *17*, 105. (f) Wilke, G. *Angew. Chem.* **1988**, *100*, 189; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185.

[2] Bogdanovic, B.; Ilmaier, B.; Walter, D.; Wilke, G.; Krüger, C.; Tsay, Y.-H. 1972. Cited in ref 1d, Figure 3.

[3] Bogdanovic, B.; Galle, J.; Hoffman, N.; Wilke, G. Unpublished (1972−1974). Cited in ref 1e, pp 113 and 127.

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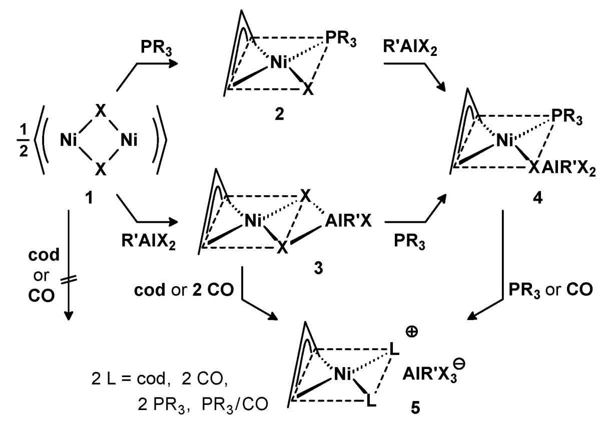
Scheme 1

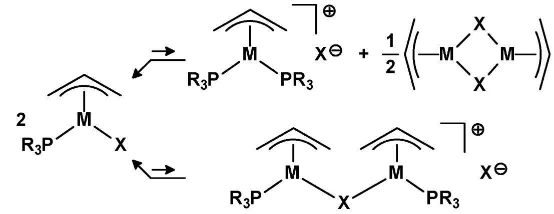


catalyzed dimerization of methylacrylate.[4] In the latter case the formation of intermediate $(\eta^3\text{-}C_3H_5)Ni(PMe_3)BF_4$ was proposed, which is closely related to **4**. Japanese authors have reported a $(\eta^3\text{-}C_3H_5)Pd(PR_3)Cl/AgY$ or TlY (Y = e.g., BF_4, PF_6, SbF_6, ClO_4) catalyzed coupling of vinylarenes with terminal alkenes. They presume that the complex anion leaves an uncoordinated site at palladium.[5] Only recently have Widenhoefer et al. suggested that the 1,6-diene cycloisomerization catalyst generated by reaction of $(\eta^3\text{-}C_3H_5)Pd(PCy_3)Cl$ with $NaB\{3,5\text{-}C_6H_3(CF_3)_2\}_4$ and $HSiEt_3$ in CH_2Cl_2 contained a potential vacant coordination site on palladium that could be occupied by some weakly coordinated ligand such as solvent, water, or silane.[6]

Despite all these studies, there is so far no compelling evidence for the occurrence of highly electron deficient, ionic 12*e* $[(\eta^3\text{-}C_3H_5)M]Y$ or 14*e* $[(\eta^3\text{-}C_3H_5)ML]Y$ complexes with a noncoordinating counterion Y,[7] but it is clear that such complexes would be of high potential interest.[8] In an attempt to synthesize complexes of the type $[(\eta^3\text{-}C_3H_5)M(PR_3)]Y$ with weakly or noncoordinating ions, such as Y = PF_6, $B(C_6F_5)_4$,[9] $B\{3,5\text{-}C_6H_3(CF_3)_2\}_4$ (TFPB, BArF),[10] or $Al\{OC(CF_3)_3\}_4$,[11] we isolated single halide-bridged, dinuclear complexes $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ (X = Cl, Br). Here we describe the structure and reactions of these compounds. We have already reported on related Pd complexes containing N-heterocyclic carbene ligands instead of phosphine.[12] Very recently, the cationic metal-pair complexes have also been the subject of a patent.[13]

Results and Discussion

While the electrical conductivity of $\{(\eta^3\text{-allyl})M(\mu\text{-}X)\}_2$ solutions is negligible, as was shown for $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2$ in benzene and DMSO/H_2O,[14] it is noticeable for $(\eta^3\text{-}C_3H_5)M(PR_3)X$ complexes (for 10^{-2} M $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)X$, X = Cl and Br, in DMSO, $\Lambda \approx 0.3\ S\cdot cm^2\cdot mol^{-1}$), suggesting slight self-ionization according to eq 2a or 2b. Ligand exchange processes of $(\eta^3\text{-}C_3H_5)M(PR_3)X$ complexes have been previously proposed, but have so far not been specified.[15] In fact, partial self-ionization according to eq 2b is also evident from the ESIpos mass spectra of the complexes $(\eta^3\text{-}C_3H_5)M(PR_3)X$ (M = Ni, Pd; R = ^{i}Pr, ^{t}Bu; X = Cl, Br, OTf), which display, besides the expected mononuclear ions $[M - X]^+$, for the P^iPr_3-ligated compounds intense signals of the dinuclear ions $[2M - X]^+$.



(2a)

(2b)

When the complexes $(\eta^3\text{-}C_3H_5)M(PR_3)X$ (X = Cl, Br) are reacted with an excess of thallium reagent TlY of a weakly coordinating anion (Y = PF_6, $B(C_6F_5)_4$, and $B\{C_6H_3(CF_3)_2\}_4$) in CH_2Cl_2 at −30 °C, only 0.5 equiv of the TlY is consumed to form TlX. The resulting products are the ionic dinuclear complexes $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ (**6**−**11**), in which the remaining halide ion bridges the two metal centers. The same products are obtained when the dinuclear $\{(\eta^3\text{-}C_3H_5)M(\mu\text{-}X)\}_2$ are reacted with a stoichiometric amount of PR_3 and TlX in a one-pot reaction. The toxic TlY reagents are preferred over the more reactive AgY reagents because of the avoidance of side-reactions. The derivatives with Y = $Al\{OC(CF_3)_3\}_4$ have been prepared by the reaction of $(\eta^3\text{-}C_3H_5)M(PR_3)X$ with $LiAl\{OC(CF_3)_3\}_4$, demonstrating also that M′X salts (M′ = Li, Tl, Ag) are readily eliminated (eq 3).

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[4] (a) Sperling, K. Dissertation (G. Wilke), Universität Bochum, Germany, 1983. (b) Wilke, G.; Sperling, K.; Stehling, L. German Patent DOS 3.336.691, 1983; US Patent 4.594.447, 1986. (c) Wilke, G. *Proc. 5th IUPAC Symp. Org. Synth. 1984*; Blackwell: Oxford; 1985; p 1.

[5] Hattori, S.; Munakata, H.; Tatsuoka, K.; Shimizu, T. US Patent 3.803.254, 1974.

[6] (a) Widenhoefer, R. A.; Perch, N. S. *Org. Lett.* **1999**, *1*, 1103. (b) Kisanga, P.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 10017. (c) Widenhoefer, R. A. *Acc. Chem. Res.* **2002**, *35*, 905.

[7] (a) Chauvin, Y.; Olivier, H. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; p 258. (b) Elschenbroich, C. *Organometallchemie*, 4th ed.; Teubner: Stuttgart, 2003; p 651.

[8] Several ionic or neutral, seemingly three-coordinate 14e Ni^{II}- and Pd^{II}-organyl complexes that feature an additional β-H agostic interaction have been described in recent years. (a) $[(^tBu_2PC_2H_4P^tBu_2)Ni(C_2H_5)][BF_4]$: Conroy-Lewis, F. M.; Mole, L.; Redhouse, A. D.; Litster, S. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1601. (b) $(R_3P)Pd(Ar)X$ (X = Br, I, OTf): Stambuli, J. P.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346. Stambuli, J. P.; Incarvito, C. D.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184. (c) $[(\alpha\text{-diimine})MR][BAr_4]$ (M = Ni, Pd; R = Et, Pr): Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539. Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068. (d) (β-diketiminate)NiR (R = Et, Pr): Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984.

[9] (a) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245. (c) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218. (d) Massey, A. G.; Park, A. J. *Organometallic Synthesis*; King, R. B.; Eisch, J. J., Eds.; Elsevier: New York, 1986; Vol. 3, p 461.

[10] (a) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn* **1984**, *57*, 2600. (b) Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545.

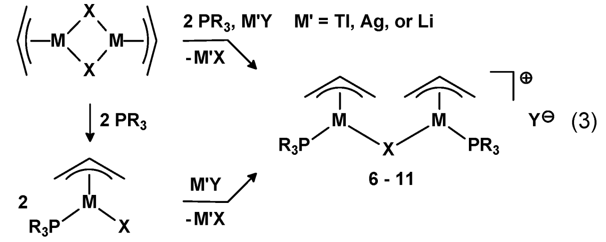
[11] $Al(OR_F)_4^-$: Barbarich, T. J.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *J. Mol. Catal.* **1998**, *128*, 289. Ivanova, S. M.; Nolan, B. G.; Kobayashi, Y.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Chem. Eur. J.* **2001**, *7*, 503. Krossing, I. *Chem. Eur. J.* **2001**, *7*, 490.

[12] Ding, Y.; Goddard, R.; Pörschke, K.-R. *Organometallics* **2005**, *24*, 439.

[13] Goodall, B. L.; Petoff, J. L.; Shen, H. US Patent Application 2005/0043494 A1.

[14] (a) Khvostik, G. M.; Poddubnyi, I. Y.; Sokolov, V. N.; Tsereteli, I. Y. *Russ. J. Phys. Chem.* **1970**, *44*, 872. (b) Khan, B. T.; Mohan, K. M.; Zakeeruddin, S. M. *Metallorg. Khim.* **1990**, *3*, 743.

[15] Vrieze, K.; MacLean, C.; Cossee, P.; Hilbers, C. W. *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 1077.

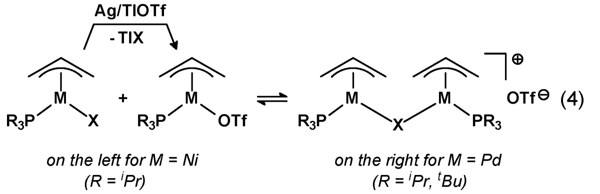


	M	R	X	Y
6a	Ni	^{i}Pr	Br	$B(C_6F_5)_4$
6b	Ni	^{i}Pr	Br	BArF
6c	Ni	^{i}Pr	Br	$Al\{OC(CF_3)_3\}_4$
7a	Ni	^{t}Bu	Br	$B(C_6F_5)_4$
7b	Ni	^{t}Bu	Br	BArF

	M	R	X	Y		M	R	X	Y
8a	Pd	^{i}Pr	Cl	PF_6	**10a**	Pd	^{i}Pr	Br	OTf
8b	Pd	^{i}Pr	Cl	$B(C_6F_5)_4$	**10b**	Pd	^{i}Pr	Br	$B(C_6F_5)_4$
8c	Pd	^{i}Pr	Cl	BArF	**10c**	Pd	^{i}Pr	Br	BArF
8d	Pd	^{i}Pr	Cl	$Al\{OC(CF_3)_3\}_4$	**10d**	Pd	^{i}Pr	Br	$Al\{OC(CF_3)_3\}_4$
9a	Pd	^{t}Bu	Cl	PF_6	**11a**	Pd	^{t}Bu	Br	OTf
9b	Pd	^{t}Bu	Cl	$B(C_6F_5)_4$	**11b**	Pd	^{t}Bu	Br	$B(C_6F_5)_4$
9c	Pd	^{t}Bu	Cl	BArF	**11c**	Pd	^{t}Bu	Br	BArF
9d	Pd	^{t}Bu	Cl	$Al\{OC(CF_3)_3\}_4$	**11d**	Pd	^{t}Bu	Br	$Al\{OC(CF_3)_3\}_4$

A special situation arises for the weakly nucleophilic trifluoromethylsulfonate (triflate, OTf) anion. The Ni complexes $(\eta^3\text{-}C_3H_5)Ni(P^iPr_3)X$ (X = Cl, Br) react with 1 equiv of TlOTf at 0 °C to give $(\eta^3\text{-}C_3H_5)Ni(P^iPr_3)(OTf)$[16a] with full replacement of the halide by the triflate anion (the P^tBu_3 derivative appears unstable at −30 °C). However, the synthesis of halide-bridged, dinuclear Ni triflates $[\{(\eta^3\text{-}C_3H_5)Ni(PR_3)\}_2(\mu\text{-}X)]OTf$ has failed, and it seems that in this case the OTf ion would attack Ni to cleave the Ni−μ-X−Ni bridge and give equal amounts of $(\eta^3\text{-}C_3H_5)Ni(PR_3)X$ and $(\eta^3\text{-}C_3H_5)Ni(PR_3)(OTf)$. In fact, from diethyl ether solutions containing equal amounts of $(\eta^3\text{-}C_3H_5)Ni(P^iPr_3)X$ and $(\eta^3\text{-}C_3H_5)Ni(P^iPr_3)(OTf)$ the two complexes crystallize unchanged at low temperature. At −80 °C the ^{1}H, ^{13}C, and ^{31}P NMR spectra of this mixture show the resonances of the individual complexes, whereas at ambient temperature equilibration occurs due to an exchange process.

In contrast, the Pd complexes $(\eta^3\text{-}C_3H_5)Pd(PR_3)Cl$ (R = ^{i}Pr, ^{t}Bu) react with an excess of TlOTf to give a mixture of the mononuclear Pd-triflates $(\eta^3\text{-}C_3H_5)Pd(PR_3)(OTf)$ (R = ^{i}Pr,[16b] ^{t}Bu) and the (nonisolated) chloride-bridged triflate salts $[\{(\eta^3\text{-}C_3H_5)Pd(PR_3)\}_2(\mu\text{-}Cl)]OTf$, while the reaction of the bromide $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Br$ with TlOTf at −30 °C stops at the stage of the dinuclear **10a**. Here, the pure $(\eta^3\text{-}C_3H_5)Pd(PR_3)(OTf)$ complexes seem only to be accessible when the more reactive AgOTf is used.[16b] Nevertheless, the reactions with an excess of TlOTf indicate that the Pd−μ-Cl−Pd bridges in the title complexes are more readily cleaved by the OTf anion than Pd−μ-Br−Pd bridges. The π-allylpalladium bromides $(\eta^3\text{-}C_3H_5)Pd(PR_3)Br$ (R = ^{i}Pr, ^{t}Bu) react with 0.5 equiv of TlOTf according to eq 3 to yield the dinuclear bromide-bridged **10a** and **11a**. These complexes were also prepared by mixing equal amounts of $(\eta^3\text{-}C_3H_5)Pd(PR_3)Br$ and $(\eta^3\text{-}C_3H_5)Pd(PR_3)OTf$ (eq 4). It appears that in $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]OTf$ complexes the OTf anion competes with the bridging halide for coordination at the metal center. Thus, eq 4 represents an equilibrium which lies on the left for Ni and on the right for Pd.



The $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ complexes **6**−**11** form yellow to red microcrystals, and only for **6c** and **11b** were we able to obtain single crystals suitable for X-ray structure analysis (see below). In general, the Pd complexes in this series are thermally more stable than the corresponding Ni complexes, and the P^iPr_3 derivatives are more stable than those containing P^tBu_3. Thus, the P^iPr_3-ligated Pd complexes **8** and **10** are stable at ambient temperature over prolonged periods, whereas the P^tBu_3-ligated Ni complexes **7** must be handled at −30 °C. The remaining complexes **6**, **9**, and **11** are briefly stable at ambient temperature.

No meaningful EI mass spectra have been obtained for **6**−**11**. In the ESIpos mass spectra (CH_2Cl_2) of the $[\{(\eta^3\text{-}C_3H_5)Ni(P^iPr_3)\}_2(\mu\text{-}Br)]^+$ complexes **6** both the dinuclear cation (*m/e* 597) and the halide-free mononuclear $[(\eta^3\text{-}C_3H_5)Ni(P^iPr_3)]^+$ (*m/e* 259, undergoing loss of H atoms) are found as prominent ions in the spectra. An even stronger peak for the dinuclear cation is found for the Pd derivatives **10**, where the dinuclear cation $[\{(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Br)]^+$ (*m/e* 693) but also $[(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)]^+$ (*m/e* 307) may represent the base ion. For the other Ni and Pd complexes, that is, when either P^iPr_3 is replaced with P^tBu_3 (**7 and 11**) and/or bromide is replaced with chloride (**8 and 9**), the base ion is mostly given by $[(\eta^3\text{-}C_3H_5)M(PR_3)]^+$, while the intensity of the dinuclear cation diminishes to 5−20%. In view of the fact that the mononuclear $(\eta^3\text{-}C_3H_5)M(PR_3)X$ and the dinuclear derivatives $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ in each case give rise to mono- and dinuclear cations in the ESIpos mass spectra, their distinction is hardly possible by this method.

Attempts to synthesize derivatives of the P^iPr_3- and P^tBu_3-ligated complexes **6**−**11** with the much smaller PMe_3 ligand were unsuccessful. Reaction of $(\eta^3\text{-}C_3H_5)M(PMe_3)X$ (M = Ni, Pd; X = Cl, Br) with TlY (Y = OTf, PF_6, $B(C_6F_5)_4$, $B\{3,5\text{-}C_6H_3(CF_3)_2\}_4$) or $LiAl\{OC(CF_3)_3\}_4$ in CH_2Cl_2 at 0 °C resulted in a redistribution of the PMe_3 ligands to yield a mixture of $[(\eta^3\text{-}C_3H_5)M(PMe_3)_2]Y$ (of which the PF_6 salts **12** and **13** have been described in the Experimental Part) and phosphine-free $\{(\eta^3\text{-}C_3H_5)M(\mu\text{-}X)\}_2$ (eq 5). It seems likely that in the course of the reaction the dinuclear $[\{(\eta^3\text{-}C_3H_5)M(PMe_3)\}_2(\mu\text{-}X)]Y$ is intermediately formed, but that it stabilizes to give the bis(phosphine) complex $[(\eta^3\text{-}C_3H_5)M(PMe_3)_2]Y$. The formation of such complexes with vicinal phosphine ligands is less favored (P^iPr_3) or even impossible (P^tBu_3) for the more bulky phosphines, which explains why for these phosphines dinuclear $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ is isolated.

There have been relatively few dinuclear M−μ-X−M (M = Ni, Pd, Pt) complexes with single halide bridges.

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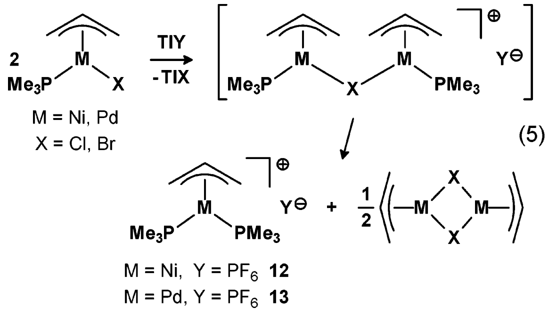
(16) (a) Proft, B. Dissertation, Universität Düsseldorf, 1993. (b) Krause, J.; Goddard, R.; Mynott, R.; Pörschke, K.-R. *Organometallics* **2001**, *20*, 1992.



(5)

The reaction of $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2$ with cyclohexanone oxime affords the neutral, asymmetrical addition compound $(\eta^3\text{-}C_3H_5)(Cl)Pd(\mu\text{-}Cl)Pd(\eta^3\text{-}C_3H_5)(C_6H_{10}NOH)$ (**A**), in which one of the initially two chloride bridges is cleaved and the other is retained.[17] Further examples are given by the ionic $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3Pd\}_2(\mu\text{-}Cl)]BF_4$ (**B**)[18] and $[\{Me_2C_2(NC_6H_3{}^iPr_2)_2PtMe\}_2(\mu\text{-}Cl)]BF_4$ (**C**),[19] for which structures with approximate C_2 point symmetry of the cation have been observed. Complexes **6**−**11** are most closely related to the concurrently reported complexes $[\{(\eta^3\text{-}C_3H_5)Pd(NHC)\}_2(\mu\text{-}X)]Y$, having carbene instead of phosphine ligands, and of which $[\{(\eta^3\text{-}C_3H_5)PdC(N({}^tBu)CH)_2\}_2(\mu\text{-}Cl)]PF_6$ (**D**) has been structurally characterized.[12]

NMR Spectra. Selected solution ^1H, ^{13}C, and ^{31}P NMR data for the neutral mononuclear $(\eta^3\text{-}C_3H_5)M(PR_3)X$ complexes and the dinuclear cations of complexes **6**−**11** in CD_2Cl_2 are listed in Table 1. More comprehensive data listings (Tables S1 and S2) are contained in the Supporting Information. Spectral data of the anions OTf (δ(C) 119.7, J(CF) = 320 Hz), $Al\{OC(CF_3)_3\}_4$ (δ(C) 120.5, J(CF) = 293 Hz), and PF_6 (δ(P) −144.7, J(PF) = 711 Hz) (at −80 °C) are not quoted further. In the cases where ^{11}B NMR spectra have been recorded, the $B(C_6F_5)_4$ anion gives rise to a resonance at δ(B) −16.7 and the BArF anion at δ(B) −6.7.

The formally square-planar mononuclear $(\eta^3\text{-}C_3H_5)M(PR_3)X$ complexes are chiral, and this gives rise to five ^1H and three ^{13}C allyl signals for the rigid structures. Similar principal resonances are expected for the dinuclear $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]^+$ cations, but these resonances, as well as those of the phosphine ligands, can be doubled due to the presence of diastereomers.[12] A detailed description of the allyl resonances of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Cl$ (in THF solution) and the factors that govern the chemical shifts and dynamic properties can be found in ref 16b.

For the $[\{(\eta^3\text{-}C_3H_5)Ni(P^iPr_3)\}_2(\mu\text{-}Br)]^+$ complexes **6** the allyl ^1H and ^{13}C NMR resonances are somewhat broadened at ambient temperature, indicative of a slow dynamic process. For the P^tBu_3-ligated **7** the spectra are very broad between ambient temperature and −30 °C, and this can be explained by the occurrence of various dynamic processes such as π−σ-allyl isomerization and phosphine dissociation. There is generally little difference between the spectra of $(\eta^3\text{-}C_3H_5)Ni(PR_3)Br$ and the dinuclear ionic derivatives $[\{(\eta^3\text{-}C_3H_5)Ni(PR_3)\}_2(\mu\text{-}Br)]Y$.

The spectra of mononuclear $(\eta^3\text{-}C_3H_5)Pd(PR_3)X$ and the corresponding dinuclear ionic complexes **8**−**11** are much better resolved than those of the Ni derivatives, and for the Pd complexes resolution increases on going from ^{t}Bu to ^{i}Pr and from Cl to Br. While in the ambient temperature ^1H NMR spectra of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)X$ (X = Cl, Br, OTf) in THF-d_8 the syn and anti allyl protons trans to X show line-broadening or coalescence due to selective π−σ-allyl rearrangement with exchange of these protons,[16b] the resonances are sharp for the CD_2Cl_2 solution and, moreover, the isopropyl Me groups are diastereotopic, indicative of a rigid chiral structure. Resolved allyl resonances and diastereotopic Me groups are also found for the dinuclear $[\{(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}X)]^+$ complexes **8** and **10** at ambient temperature, and this can be taken as evidence for an essentially nondynamic coordination of the ligands at the Pd centers. For the $[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}X)]^+$ complexes **9** and **11** well-resolved spectra are observed at −30 °C, whereas resonances are broad at ambient temperature.

If one compares the ^1H and ^{13}C NMR spectra of the $[\{(\eta^3\text{-}C_3H_5)Pd(PR_3)\}_2(\mu\text{-}X)]^+$ cations with those of the neutral $(\eta^3\text{-}C_3H_5)Pd(PR_3)X$ precursors, there is a distinct shift of the allyl resonances to lower field. However, the shift differences between the $[\{(\eta^3\text{-}C_3H_5)Pd(PR_3)\}_2(\mu\text{-}X)]^+$ cations bearing the same phosphine are only marginal for the different halides (Cl vs Br). Comparison of the shift data and the dynamic properties of the various complexes leads us to conclude that (a) in $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)X$ the donor strength of bromide toward Pd is greater than that of chloride, in agreement with the lower electronegativity and the larger polarizability of bromide, (b) the donor strength of the halide toward Pd is weaker in the dinuclear complexes than in the corresponding mononuclear complexes, and (c) the allyl groups are more tightly coordinated in the (dinuclear) cationic complexes than in the (mononuclear) neutral compounds.

For an individual cation of the $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ complexes the allyl and PR_3 resonances are, as expected, rather independent of Y, but this is not always the case. In particular, the OTf and BArF salts are sometimes at marked variance to the other complexes of the series (see in Table S2, for instance, complexes **11a** and **11c** versus **11b**,**d**). It appears that ion-pairing is significant in solution and that the BArF anion imposes an anisotropic effect on the cation. In the case of the OTf complexes ion-pairing should foster the equilibrium process according to eq 4, which explains for **11a** the deviations from the expected resonances.

When the temperature is lowered from 25 to −30 or −80 °C, the $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ complexes, for which at least two of the stabilizing parameters Pd > Ni, $^iPr_3P$ > $^tBu_3P$, and Br > Cl are fulfilled and, hence, relatively rigid structures around the metal centers with enantiomeric stability can be assumed, show a splitting of the allyl ^1H and ^{13}C resonances. The effect is most obvious for the syn proton trans to P and both anti protons (but not for the syn proton trans to halide), the meso carbon, and the methylene carbon trans to P. Moreover, in the ^{31}P NMR spectra the singlet is split into two very close lines of equal intensity. While for most complexes the effect has been observed at −80 °C, it is found for most BArF salts already at −30 °C (**9c**,

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[17] The Pd−Cl−Pd angle in **A** is 107.3°. Kitano, Y.; Kajimoto, T.; Kashiwagi, M.; Kinoshita, Y. *J. Organomet. Chem.* **1971**, *33*, 123.

[18] The Pd−Cl−Pd angle in **B** is 134.8°. Terheijden, J.; van Koten, G.; Grove, D. M.; Vrieze, K.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1987**, 1359.

[19] Albano, V. G.; Di Serio, M.; Monari, M.; Orabona, I.; Panunzi, A.; Ruffo, F. *Inorg. Chem.* **2002**, *41*, 2672.

Table 1. NMR Data of Selected [{(η^3-C_3H_5)M(PR_3)}$_2$(μ-X)]Y Complexes 6−11 and of Reference Compounds[a]

	Allyl					PR$_3$				
	δ(H)			δ(C)		δ(H)		δ(C)		
	H_{meso}	H_{syn}	H_{anti}	C_{meso}	C_{term}	PCH	Me	PC	Me	δ(P)
(C_3H_5)Ni(P^iPr_3)Br	5.24[c]	3.95, 2.85[c]	2.87, 1.79[c]	108.3	74.1, 46.8	2.32	1.33, 1.28	24.8	19.9	39.8[c]
6a[c] (Y = B(C_6F_5)$_4$)	5.35	4.29, 3.07	2.98, 2.01	110.2	74.9, 49.2	2.16	1.22, 1.18	22.9	18.2, 18.1	39.5, 39.3
(C_3H_5)Ni(P^tBu_3)Br[c]	5.22	3.80, 3.70	2.95, 1.86	104.1	71.6, 51.6		1.45	38.3	32.3[b]	70.1
7b[b] (Y = BArF)		*d*			d		1.69	37.2	30.0	61.6
(C_3H_5)Pd(P^iPr_3)Cl	5.41	4.53, 3.54	3.53, 2.61	116.5	80.2, 51.2	2.41	1.29, 1.24	25.0	20.0, 19.9	53.3
8b[c] (Y = B(C_6F_5)$_4$)	5.50	4.57, 3.52	3.60, 2.77	117.8	82.7, 52.5	2.28	1.17	24.0	19.0, 18.9	51.6, 51.5
(C_3H_5)Pd(P^tBu_3)Cl[c]	5.42	4.51, 4.13	3.67, 2.78	113.6	81.9, 57.5		1.40	38.5	33.8, 27.6	82.5
9b[b] (Y = B(C_6F_5)$_4$)	5.53	4.69, 4.33	3.83, 2.98	115.2	86.3, 58.1		1.45	39.3	32.3	85.0
(C_3H_5)Pd(P^iPr_3)Br	5.37	4.58, 3.74	3.46, 2.70	116.0	79.4, 54.4	2.45	1.29, 1.24	25.4	20.0	52.9
10b[c] (Y = B(C_6F_5)$_4$)	5.45	4.58, 3.71	3.51, 2.88	117.5	81.4, 55.9	2.33	1.20, 1.18	24.4	19.1, 19.0	51.2, 51.1
(C_3H_5)Pd(P^tBu_3)Br[b]	5.34	4.61, 4.33	3.60, 2.89	112.7	81.0, 61.4		1.46	39.0	32.5	85.7
11b[c] (Y = B(C_6F_5)$_4$)	5.43	4.69, 4.55	3.65, 3.05	113.8	84.0, 62.0		1.41	38.7	34.3, 27.4	84.8, 84.7

[a] Solvent CH_2Cl_2. Temperature 25 °C. For those ^1H and ^{13}C resonances that are split due to the resolution of diastereomers mean values of the chemical shifts are given. Sh = sharp, br = broad. [b] Temperature −30 °C. [c] Temperature −80 °C. [d] The ^1H and ^{13}C allyl resonances of the compounds are broad between −30 and 20 °C.

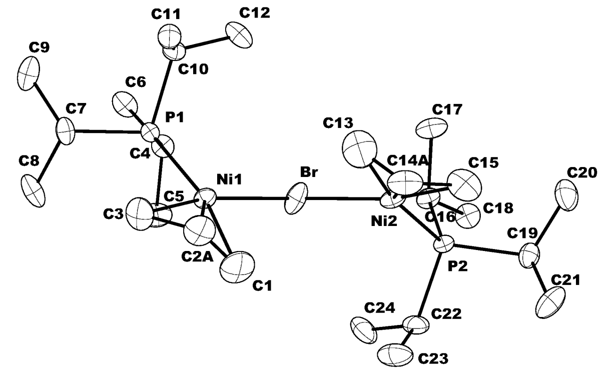

Figure 1. Cation of **6c**, viewed down the approximate 2-fold axis of symmetry passing through the Br atom and the midpoint between Ni1 and Ni2. Selected distances (Å), angles (deg), and torsion angles (deg): Ni1−Br = 2.3564(5), Ni2−Br = 2.3674(5), Ni1−P1 = 2.2248(8), Ni2−P2 = 2.2244(7), Ni1−C1 = 2.048(4), Ni1−C2A = 1.998(5), Ni1−C3 = 1.992(3), Ni2−C13 = 2.051(3), Ni2−C14A = 1.972(4), Ni2−C15 = 1.997(4); Ni1−Br−Ni2 = 118.01(2), Br−Ni1−P1 = 97.75(2), Br−Ni2−P2 = 94.53(2); Ni1−Br−Ni2−P2 = 154(1), Ni2−Br−Ni1−P1 = 140(1).

10c, and **11c**). The splittings can be attributed to the presence of diastereomers arising from enantiomerically stable chiral centers. A similar observation has been made for the Pd derivatives with NHC ligands instead of phosphines, and the phenomenon is discussed in ref 12 in more detail.

Crystal Structures of 6c and 11b. The structure of the nickel complex **6c** and that of the palladium complex **11b** have been determined by single-crystal X-ray analysis at 100 K (Tables S3−S10 and Figures S1 and S2 in the Supporting Information). Both compounds are found to exist as discrete dinuclear cations and Al{OC(CF_3)$_3$}$_4$ or B(C_6F_5)$_4$ anions.

The structure of the cation of **6c** is shown in Figure 1. Despite an asymmetrical environment caused by the crystal, which is chiral, the central part of the cation (the two allyl groups, the two Ni and two P atoms, as well as the Br atom) exhibits an approximate 2-fold axis of symmetry (rms deviation 0.16 Å) that passes through the Br atom and the midpoint of the two Ni atoms. The coordination planes of the two Ni atoms are planar (rms deviation: 0.06 Å (C1,C2,Ni1,Br,P1); 0.04 Å (C13,C15,Ni2,Br,P2)), and they make an angle of 119° to one another. The high symmetry is broken by the isopropyl groups on the P atoms, which are rotated by 11° to one another with respect to the 2-fold axis, presumably due to packing forces, since the isopropyl groups on the two P atoms are well separated.

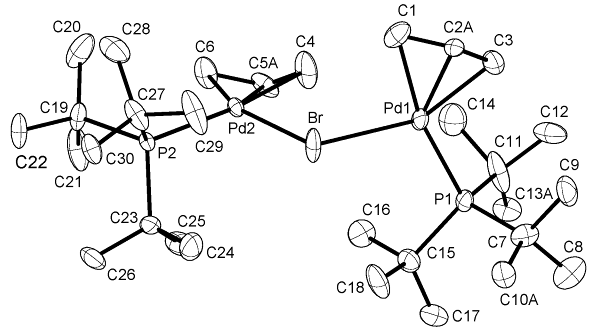

Figure 2. Structure of the cation of **11b**. Selected bond distances (Å), angles (deg), and dihedral angles (deg): Pd1−C1 = 2.207(4), Pd1−C3 = 2.133(4), Pd1−P1 = 2.407(1), Pd1−Br = 2.5431(4), Pd2−C4 = 2.190(4), Pd2−C6 = 2.151(4), Pd2−P2 = 2.409(1), Pd2−Br = 2.5511(4); Pd1−Br−Pd2 = 119.63(2), P1−Pd1−Br = 107.26(3), C1−Pd1−P1 = 167.5(1), C3−Pd1−Br = 151.4(1), P2−Pd2−Br = 101.61(2), C4−Pd2−P2 = 169.7(1), C6−Pd2−Br = 154.2(1); P1,Pd1,Br,C1,C3/P2,Pd2,Br,C4,C6 = 92.8(1), P1,Pd1,Br,C1,C3/Pd1,Br,Pd2 = 97.9(1), P2,Pd2,Br,C4,C6/Pd1,Br,Pd2 = 5.8(1).

Figure 2 shows the structure of the cation of **11b**, which is made up of two [(η^3-C_3H_5)Pd(P^tBu_3)] moieties bridged likewise by a bromide ion. The meso C atoms of the allyl groups are disordered equally over two positions in the cation. Since the allyl groups create stereogenic centers at Pd1 and Pd2, we must assume that the crystal is composed of diastereomeric cations. The Pd1−Br−Pd2 angle at 119.63(2)° is within the range of observed Pd−Cl−Pd angles for the comparable complexes **A** and **B**.[17,18] Pd−Br−Pd angles of up to 180° are found in other complexes.[20]

Although the cation in **11b** could in principle exhibit C_s or C_2 point symmetry (C_i is impossible on account of the nonlinear Pd1−Br−Pd2 bond), it in fact adopts a geometry with C_1 symmetry, such that the coordination

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(20) (a) Usón, R.; Forniés, J.; Tomás, M.; Menjón, B.; Welch, A. J. *Organometallics* **1988**, *7*, 1318. (b) Martin, R.; Keller, H. J.; Müller, B. *Z. Naturforsch. B.: Chem. Sci.* **1985**, *40*, 57.

plane of Pd2 and the plane Pd2,Br,Pd1 are approximately coplanar; that is, Pd1 lies approximately in the coordination plane of Pd2, and the coordination plane of Pd1 lies approximately perpendicular (92.83(6)°) to it. As a result, the coordination planes of the two Pd atoms are almost perpendicular to one another at bromine. The bonding of the M−X−M core of the Pd-bromide **11b** thus appears distinctly different from that of the Ni-bromide **6c** and the Pd/Pt-chlorides **A**−**D**.

The mean Pd−Br bond length of 2.547(1) Å in **11b** is only slightly longer than that in known Pd-allyl complexes with terminal Pd−Br bonds (2.51 Å),[21] despite the bridging position of the bromine atom. This may be due predominantly to the partial positive charge at the Pd centers, which should strengthen the Pd−Br bonds and lead to shortening, whereas possible $p\pi-d\pi$ bonding should affect both Pd−Br bonds with terminal and with bridging Br atoms. The mean lengths of the Pd−P bonds at 2.408(1) Å in the cation of **11b** are substantially longer than for the related neutral (π-allyl)Pd(PR_3)Br complexes (2.25−2.33 Å).[21a,c]

Conclusions

The reactions described here shed light on the broadly held opinion that the reaction of (η^3-allyl)M(PR_3)X complexes (M = Ni, Pd; X = halide) with AgY or TlY reagents of noncoordinating anions Y generates coordinatively unsaturated complexes [(η^3-allyl)M(PR_3)]Y. We show that under the conditions of such experiments dinuclear ionic complexes $[\{(\eta^3\text{-}C_3H_5)M(PR_3)\}_2(\mu\text{-}X)]Y$ are formed, and these contain a strong central M−μ-X−M linkage that is not cleaved by additional Ag/TlY in the absence of donor ligands.

Experimental Part

All manipulations were carried out under argon using Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$ or P_4O_{10}. $\{(\eta^3\text{-}C_3H_5)Ni(\mu\text{-}X)\}_2$[22] and $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}X)\}_2$[23] (X = Cl, Br, I), $TlB\{3,5\text{-}C_6H_3(CF_3)_2\}_4$,[24] $TlB(C_6F_5)_4$,[25] $LiAl\{OC(CF_3)_3\}_4$,[11] and P^tBu_3[26] were prepared according to the literature. $AgPF_6$, AgOTf, and $TlPF_6$ were obtained from Aldrich, and TlOTf was prepared by reacting Tl_2CO_3 with HOTf. Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. EI mass spectra were recorded at 70 eV; ESIpos mass spectra refer to ^{35}Cl, ^{58}Ni, ^{79}Br, and ^{106}Pd. Solution ^{1}H NMR spectra were measured at 300 MHz, ^{13}C NMR spectra at 75.5 MHz (both relative to TMS), and ^{31}P NMR spectra at 121.5 MHz (relative to external 85% aqueous H_3PO_4) on Bruker AMX-300 and DPX-300 instruments.

(η^3-C_3H_5)Ni(P^iPr_3)Cl. A yellow-brown solution of $\{(\eta^3\text{-}C_3H_5)Ni(\mu\text{-}Cl)\}_2$ (406 mg, 3.00 mmol Ni) and P^iPr_3 (480 mg, 3.00 mmol) in 20 mL of diethyl ether was stirred at 0 °C for a few minutes. Cooling the mixture from −60 to −78 °C afforded large yellow-brown crystals, which were freed from the mother liquor by cannulation, washed with some cold pentane (−78 °C), and dried under vacuum (−20 °C): yield 680 mg (77%). For NMR data, see Table S1. $C_{12}H_{26}ClNiP$ (295.5).

(η^3-C_3H_5)Ni(P^iPr_3)Br.[27] A deep red solution of $\{(\eta^3\text{-}C_3H_5)Ni(\mu\text{-}Br)\}_2$ (1.80 g, 10.0 mmol Ni) in 50 mL of diethyl ether was stirred with P^iPr_3 (1.60 g, 10.0 mmol) at 0 °C. The solution was cooled below −40 °C to give small yellow-brown crystals, which were separated as described above: yield 2.28 g (67%). EI-MS (55 °C): *m/e* (%) 338 ($[M]^+$, 15), 201 ($[^iPr_3PC_3H_5]^+$, 100). ESIpos-MS (CH_2Cl_2): *m/e* (%) 597 ($[2M - Br]^+$, 100). For NMR data, see Table 1. $C_{12}H_{26}BrNiP$ (339.9).

(η^3-C_3H_5)Ni(P^iPr_3)OTf.[16a] A solution of (η^3-C_3H_5)Ni(P^iPr_3)Cl (296 mg, 1.00 mmol) or (η^3-C_3H_5)Ni(P^iPr_3)Br (340 mg, 1.00 mmol) in 10 mL of diethyl ether was stirred with solid TlOTf (354 mg, 1.00 mmol) at 0 °C for 30 min. After removal of the precipitated TlX by filtration the solution was cooled below −60 °C to give brown crystals: yield 225 mg (55%). EI-MS (80 °C): *m/e* (%) 408 ($[M]^+$, 5), 367 ($[M - C_3H_5]^+$, 5), 325 ($[(^iPr_2PH)Ni(OTf)]^+$, 10). ESIpos-MS (CH_2Cl_2): *m/e* (%) 667 ($[2M - OTf]^+$, 15), 259 ($[M - OTf]^+$, 80). For NMR data, see Table S1. Anal. Calcd for $C_{13}H_{26}F_3NiO_3PS$ (409.1). C, 38.17; H, 6.41; F, 13.93; Ni, 14.35; O, 11.73; P, 7.57; S, 7.84. Found: C, 38.06; H, 6.34; F, 14.11; Ni, 14.42; P, 7.51; S, 7.74. The isolated product is unstable at ambient temperature.

(η^3-C_3H_5)Ni(P^tBu_3)Cl. $\{(\eta^3\text{-}C_3H_5)Ni(\mu\text{-}Cl)\}_2$ (406 mg, 3.00 mmol Ni) was reacted with P^tBu_3 (606 mg, 3.00 mmol) in 30 mL of diethyl ether at −30 °C. Cooling below −60 °C afforded brown crystals: yield 530 mg (52%). EI-MS and ESIpos-MS: the compound decomposed. For NMR data, see Table S1. The complex appears unstable in solution and as a solid above −30 °C, forming a green solid. $C_{15}H_{32}ClNiP$ (337.5).

(η^3-C_3H_5)Ni(P^tBu_3)Br. Synthesis was as described above, but reacting $\{(\eta^3\text{-}C_3H_5)Ni(\mu\text{-}Br)\}_2$ (1.80 g, 10.0 mmol Ni) with P^tBu_3 (2.02 g, 10.0 mmol) in 50 mL of diethyl ether at −30 °C to give dark red crystals: yield 2.29 g (60%). EI-MS and ESIpos-MS: the compound decomposed. For NMR data, see Table 1. The complex appears unstable in solution above −30 °C, forming a green solid. $C_{15}H_{32}BrNiP$ (382.0).

(η^3-C_3H_5)Pd(P^iPr_3)Cl.[6b] For the synthesis and properties, see ref 16b. NMR data of the CH_2Cl_2 solution are included in Table 1. $C_{12}H_{26}ClPPd$ (343.2).

(η^3-C_3H_5)Pd(P^iPr_3)Br. Synthesis was as described above, but reacting a yellow solution of $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Br)\}_2$ (2.27 g, 10.0 mmol Pd) with P^iPr_3 (1.60 g, 10.0 mmol) in 15 mL of THF at ambient temperature. Cooling to −60 °C gave pale yellow crystals, which were isolated as described and dried under vacuum (20 °C): yield 2.91 g (75%). EI-MS (85 °C): *m/e* (%) 386 ($[M]^+$, 15), 345 ($[M - C_3H_5]^+$, 5), 306 ($[M - HBr]^+$, 10), 265 ($[M - C_3H_5 - HBr]^+$, 20). ESIpos-MS (CH_2Cl_2): *m/e* (%) 693 ($[2M - Br]^+$, 100), 307 ($[M - Br]^+$, 100). For NMR data, see Table 1. $C_{12}H_{26}BrPPd$ (387.6).

(η^3-C_3H_5)Pd(P^iPr_3)OTf. For the synthesis from (η^3-C_3H_5)Pd(P^iPr_3)Cl and AgOTf and for the NMR properties of the THF solution, see ref 16b. NMR data of the CH_2Cl_2 solution are included in Table S1. $C_{13}H_{26}F_3O_3PPdS$ (456.8). Clean synthesis of the complex seems impossible from (η^3-C_3H_5)Pd(P^iPr_3)Br at ambient temperature, and reaction with TlOTf at lower

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(21) (a) Kühn, A.; Burschka, C.; Werner, H. *Organometallics* **1982**, *1*, 496. (b) Khan, B. T.; Mohan, K. M.; Khan, S. R. A.; Venkatasubramanian, K.; Satyanarayana, T. *Polyhedron* **1996**, *15*, 63. (c) Nelson, S. G.; Hilfiker, M. A. *Org. Lett.* **1999**, *1*, 1379.

(22) Wilke, G.; Bogdanovic, B. *Angew. Chem.* **1961**, *73*, 756. Wilke, G. *Angew. Chem.* **1963**, *75*, 10; *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 105. Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kröner, M.; Oberkirch, W.; Tanaka, K.; Steinrücke, E.; Walter, D.; Zimmermann, H. *Angew. Chem.* **1966**, *78*, 157; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151. Bönnemann, H.; Bogdanovic, B.; Wilke, G. *Angew. Chem.* **1967**, *77*, 817; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 804. Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Vol. 1, p 345. Wilke, G. (Studiengesellschaft Kohle m. b. H.), Ger. Patent 1,194,417, 1965. Wilke, G. (Studiengesellschaft Kohle m. b. H.), U.S. Patent 3,468,921, 1969.

(23) (a) Smidt, J.; Hafner, W. *Angew. Chem.* **1959**, *71*, 284. Hüttel, R.; Kratzer, J. *Angew. Chem.* **1959**, *71*, 456. Moiseev, I. I.; Fedorovskaya, E. A.; Syrkin, Y. K. *Zh. Neorg. Khim.* **1959**, *4*, 2641. (b) Fischer, E. O.; Bürger, G. *Z. Naturforsch. B* **1961**, *16*, 702. (c) Shaw, B. L.; Sheppard, N. *Chem. Ind.* **1961**, 517. (d) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585. (e) Gubin, S. P.; Rubezhov, A. Z.; Winch, B. L.; Nesmeyanov, A. N. *Tetrahedron Lett.* **1964**, *39*, 2881. (f) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.

(24) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Inorg. Chem.* **1997**, *36*, 1726.

(25) Alberti, D.; Pörschke, K.-R. *Organometallics* **2004**, *23*, 1459.

(26) Fild, M.; Stelzer, O.; Schmutzler, R. *Inorg. Synth.* **1973**, *14*, 4.

(27) Wilke, G. Ger. Patent 1 793 788, 1977.

temperature (−30 °C) affords dinuclear **10a**. ESIpos-MS (CH_2Cl_2): *m/e* (%) 764 ([2M − OTf]$^+$, 40), 307 ([M − OTf]$^+$, 100).

(η^3-C_3H_5)Pd(P^tBu_3)Cl.[28] A yellow solution of {(η^3-C_3H_5)Pd(μ-Cl)}$_2$ (1.83 g, 10.0 mmol Pd) and P^tBu_3 (2.02 g, 10.0 mmol) in 15 mL of THF was stirred (20 °C). Cooling to −60 °C gave yellow crystals, which were isolated and dried under vacuum (20 °C): yield 3.39 g (88%). EI-MS: the compound decomposed. ESIpos-MS (CH_2Cl_2): *m/e* (%) 733 ([2M − Cl]$^+$, 15), 349 ([M − Cl]$^+$, 100). For NMR data, see Table 1. $C_{15}H_{32}ClPPd$ (385.3).

(η^3-C_3H_5)Pd(P^tBu_3)Br. The synthesis of this complex has to be carried out at low temperature to avoid the formation of [$^tBu_3PC_3H_5$]$^+$[(η^3-C_3H_5)$PdBr_2$]$^-$ as a brown solid and nonisolated [Pd(P^tBu_3)]. A solution of {(η^3-C_3H_5)Pd(μ-Br)}$_2$ (2.27 g, 10.0 mmol Pd) in 10 mL of CH_2Cl_2 was reacted with P^tBu_3 (2.02 g, 10.0 mmol) at −30 °C. After evaporation of the solvent the residue was dissolved in 10 mL of THF. Cooling to −60 °C gave yellow crystals: yield 3.70 g (86%). EI-MS: the compound decomposed. ESIpos-MS (CH_2Cl_2): *m/e* (%) 777 ([2M − Br]$^+$, 10), 349 ([M − Br]$^+$, 100). For NMR data, see Table 1. $C_{15}H_{32}BrPdP$ (429.7). The complex needs to be stored at −30 °C.

(η^3-C_3H_5)Pd(P^tBu_3)OTf. A solution of (η^3-C_3H_5)Pd(P^tBu_3)Cl (385 mg, 1.00 mmol) in 20 mL of CH_2Cl_2 was stirred with solid AgOTf (257 mg, 1.00 mmol) at −30 to 0 °C for 1 h. After removal of the precipitated AgCl by filtration (0 °C) the solution was concentrated under vacuum to half the volume and an equal amount of diethyl ether was added. Cooling the solution to −78 °C afforded yellow crystals: yield 390 mg (78%). EI-MS (125 °C): *m/e* (%) 349 ([M − OTf]$^+$, 1). ESIpos-MS (CH_2Cl_2): *m/e* (%) 349 ([M − OTf]$^+$, 100). For NMR data, see Table S1. $C_{16}H_{32}F_3O_3PPdS$ (498.9). The compound dissolves only poorly in diethyl ether.

[{(η^3-C_3H_5)Ni(P^iPr_3)}$_2$(μ-Br)][B(C_6F_5)$_4$] (6a). A brown solution of (η^3-C_3H_5)Ni(P^iPr_3)Br (340 mg, 1.00 mmol) in 15 mL of diethyl ether was stirred with solid TlB(C_6F_5)$_4$ (442 mg, 0.50 mmol) at −30 °C for 1 h. After removal of the precipitated TlBr the solution was concentrated to a volume of about 7 mL and about 3 mL of pentane was added. Cooling the solution to −78 °C afforded orange crystals, which were freed from the mother liquor by cannulation, washed with a small volume of cold pentane (−78 °C), and dried under vacuum (−30 °C): yield 130 mg (20%). (Full evaporation of the solvent leaves an oil, and the addition of larger amounts of pentane to an ethereal solution causes also the separation of an oil. These difficulties explain the low yield of crystalline product.) ESIpos-MS (CH_2Cl_2): *m/e* 597 ([{(C_3H_5)Ni(P^iPr_3)}$_2$(μ-Br)]$^+$, 10). ESIneg-MS (CH_2Cl_2): *m/e* 679 ([$C_{24}BF_{20}$]$^-$, 100). For NMR data, see Tables 1 and S2. $C_{24}H_{52}BrNi_2P_2\cdot C_{24}BF_{20}$ (1278.95). The complex is very soluble in the usual solvents.

[{(η^3-C_3H_5)Ni(P^iPr_3)}$_2$(μ-Br)][B{3,5-C_6H_3(CF_3)$_2$}$_4$] (6b). A solution of (η^3-C_3H_5)Ni(P^iPr_3)Br (680 mg, 2.00 mmol) in 10 mL of CH_2Cl_2 was stirred with solid TlB{3,5-C_6H_3(CF_3)$_2$}$_4$ (1.067 g, 1.00 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration. After evaporation of the solvent under vacuum the residue was dissolved in 5 mL of diethyl ether. Cooling the solution to −78 °C gave a brown precipitate, which was isolated as described above: yield 1.16 g (79%). ESIpos-MS (CH_2Cl_2): *m/e* 597 ([{(C_3H_5)Ni(P^iPr_3)}$_2$(μ-Br)]$^+$, 100). ESIneg-MS (CH_2Cl_2): *m/e* 863 ([$C_{32}H_{12}BF_{24}$]$^-$, 100). For NMR data, see Table S2. Anal. Calcd for $C_{24}H_{52}BrNi_2P_2\cdot C_{32}H_{12}BF_{24}$ (1463.1): C, 45.97; H, 4.41; B, 0.74; Br, 5.46; F, 31.16; Ni, 8.02; P, 4.23. Found: C, 45.25; H, 4.06; Ni, 7.87; P, 4.25.

[{(η^3-C_3H_5)Ni(P^iPr_3)}$_2$(μ-Br)][Al{OC(CF_3)$_3$}$_4$] (6c). A solution of (η^3-C_3H_5)Ni(P^iPr_3)Br (680 mg, 2.00 mmol) in 10 mL of CH_2Cl_2 was stirred with solid LiAl{OC(CF_3)$_3$}$_4$ (974 mg, 1.00 mmol) at −30 °C for 1 h. The off-white precipitate of LiBr was removed by filtration. The solution was concentrated to a volume of about 1 mL (full evaporation of the solvent leaves an oily residue), and a small amount of pentane (about 2 mL) was added dropwise, preventing the separation of an oily phase. Cooling the solution to −78 °C gave well-shaped brown crystals, which were isolated as described above: yield 890 mg (57%). (The product was soluble in diethyl ether but did not crystallize from it. Addition of pentane caused the separation of an oily product phase.) ESIpos-MS (CH_2Cl_2): *m/e* 597 ([{(C_3H_5)Ni(P^iPr_3)}$_2$(μ-Br)]$^+$). ESIneg-MS (CH_2Cl_2): *m/e* 967 ([$C_{16}AlF_{36}O_4$]$^-$, 100). For NMR data, see Table S2. $C_{24}H_{52}BrNi_2P_2\cdot C_{16}AlF_{36}O_4$ (1567.0).

X-ray Crystal Structure Analysis of 6c. Crystal data: [$C_{24}H_{52}BrNi_2P_2$][$C_{16}AlF_{36}O_4$], from dichloromethane/pentane, M_r = 1567.07, crystal size 0.05 × 0.13 × 0.15 mm; a = 15.0314(3) Å, b = 17.5337(2) Å, c = 22.1486(4) Å, V = 5837.4(2) Å^3, T = 100 K, orthorhombic, space group $P2_12_12_1$ (No. 19), Z = 4, d_{calcd} = 1.783 g cm^{-3}, $F(000)$ = 3128, Nonius KappaCCD diffractometer, λ(Mo Kα) = 0.71073 Å, μ = 1.55 mm^{-1}, 79 757 measured and 18 529 independent reflections (R_{int} = 0.069), 15 253 with $I > 2\sigma(I)$, θ_{max} = 30.98°, T_{min} = 0.831, T_{max} = 0.932, direct methods (*SHELXS-97*) and least-squares refinement (*SHELXL-97*) on F_o^2, both programs from G. Sheldrick, University of Göttingen, 1997; 795 parameters. The meso atoms of the η^3-allyl groups attached to Pd are disordered over two positions (70:30), H atoms riding, Chebyshev weights, R_1 = 0.0427 ($I > 2\sigma(I)$), wR_2 = 0.0814 (all data), Flack parameter = −0.008(5), $\Delta\rho_{max/min}$ = 0.951/−0.745 e Å^{-3} (0.73/0.70 Å from Br).

[{(η^3-C_3H_5)Ni(P^tBu_3)}$_2$(μ-Br)][B(C_6F_5)$_4$] (7a). A deep red solution of (η^3-C_3H_5)Ni(P^tBu_3)Br (1.91 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid TlB(C_6F_5)$_4$ (2.21 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration. The solution was cooled to −78 °C to give red crystals, which were isolated as described above: yield 3.20 g (94%). For NMR data, see Table S2. $C_{30}H_{64}BrNi_2P_2\cdot C_{24}BF_{20}$ (1363.1).

[{(η^3-C_3H_5)Ni(P^tBu_3)}$_2$(μ-Br)][B{3,5-C_6H_3(CF_3)$_2$}$_4$] (7b). A solution of (η^3-C_3H_5)Ni(P^tBu_3)Br (1.91 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid TlB{3,5-C_6H_3(CF_3)$_2$}$_4$ (2.67 g, 2.50 mmol) at −30 °C for 1 h. After removal of the TlBr an equal amount of pentane was added and the solution was cooled to −78 °C to give deep red crystals, which were isolated as described above: yield 3.33 g (86%). For NMR data, see Tables 1 and S2. $C_{30}H_{64}BrNi_2P_2\cdot C_{32}H_{12}BF_{24}$ (1547.3).

[{(η^3-C_3H_5)Pd(P^iPr_3)}$_2$(μ-Cl)][PF_6] (8a). A yellow solution of (η^3-C_3H_5)Pd(P^iPr_3)Cl (1.71 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlPF_6$ (0.87 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlCl was removed by filtration. The solution was cooled to −78 °C to give a light yellow precipitate, which was isolated as described above: yield 1.45 g (73%). ESIpos-MS (CH_2Cl_2): *m/e* 649 ([{(C_3H_5)Pd(P^iPr_3)}$_2$(μ-Cl)]$^+$), 307 ([(C_3H_5)Pd(P^iPr_3)]$^+$). For NMR data, see Table S2. Anal. Calcd for $C_{24}H_{52}ClP_2Pd_2\cdot F_6P$ (795.9): C, 36.22; H, 6.59; Cl, 4.45; P, 11.68; Pd, 26.74. Found: C, 36.31; H, 6.48; Cl, 4.45; P, 11.61; Pd, 26.60.

[{(η^3-C_3H_5)Pd(P^iPr_3)}$_2$(μ-Cl)][B(C_6F_5)$_4$] (8b). A solution of (η^3-C_3H_5)Pd(P^iPr_3)Cl (1.71 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid TlB(C_6F_5)$_4$ (2.21 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlCl was removed by filtration. The solution was cooled to −78 °C to give a yellow precipitate, which was isolated as described above: yield 1.73 g (52%). ESIpos-MS (CH_2Cl_2): *m/e* 649 ([{(C_3H_5)Pd(P^iPr_3)}$_2$(μ-Cl)]$^+$), 307 ([(C_3H_5)Pd(P^iPr_3)]$^+$). For NMR data, see Tables 1 and S2. $C_{24}H_{52}ClP_2Pd_2\cdot C_{24}BF_{20}$ (1330.0).

[{(η^3-C_3H_5)Pd(P^iPr_3)}$_2$(μ-Cl)][B{3,5-C_6H_3(CF_3)$_2$}$_4$] (8c). A solution of (η^3-C_3H_5)Pd(P^iPr_3)Cl (1.71 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid TlB{3,5-C_6H_3(CF_3)$_2$}$_4$ (2.67 g, 2.50 mmol) at −30 °C for 1 h. After removal of the TlCl the solution was concentrated in a vacuum to a volume of 5 mL. Cooling the solution below −78 °C afforded a light yellow precipitate, which was isolated as described above: yield 3.37 g (89%). ESIpos-MS (CH_2Cl_2): *m/e* 649 ([{(C_3H_5)Pd(P^iPr_3)}$_2$(μ-Cl)]$^+$), 307 ([(C_3H_5)Pd(P^iPr_3)]$^+$). For NMR data, see Table

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[28] Carturan, G.; Strukul, G. *J. Organomet. Chem.* **1978**, *157*, 475.

S2. Anal. Calcd for $C_{24}H_{52}ClP_2Pd_2{\cdot}C_{32}H_{12}BF_{24}$ (1514.1): C, 44.42; H, 4.26; B, 0.71; Cl, 2.34; P, 4.09; Pd, 14.06. Found: C, 43.85; H, 4.48; B, 0.92; Cl, 2.20; P, 3.89; Pd, 13.39.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Cl)][Al\{OC(CF_3)_3\}_4]$ (8d). A solution of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Cl$ (1.71 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $LiAl\{OC(CF_3)_3\}_4$ (2.44 g, 2.50 mmol) at −30 °C for 1 h. The off-white precipitate of LiCl was removed by filtration. The solution was cooled to −78 °C to give a beige precipitate, which was isolated as described above: yield 1.03 g (29%). ESIpos-MS (CH_2Cl_2): *m/e* 649 ($[\{(C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Cl)]^+$). For NMR data, see Table S2. $C_{24}H_{52}ClP_2Pd_2{\cdot}C_{16}AlF_{36}O_4$ (1618.0).

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)][PF_6]$ (9a). A yellow solution of $(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)Cl$ (1.93 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlPF_6$ (0.87 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlCl was removed by filtration. CH_2Cl_2 was evaporated under vacuum to leave a yellow oil, which was dissolved again in 2 mL of THF. After addition of 8 mL of diethyl ether yellow microcrystals formed very slowly at −78 °C, which were isolated as described above: yield 1.61 g (73%). ESIpos-MS (CH_2Cl_2): *m/e* 733 ($[\{(C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)]^+$), 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$). For NMR data, see Table S2. Anal. Calcd for $C_{30}H_{64}ClP_2Pd_2{\cdot}F_6P$ (880.0): C, 40.94; H, 7.33; Cl, 4.03; P, 10.56; Pd, 24.19. Found: C, 40.50; H, 6.71; Cl, 4.06; P, 10.77; Pd, 24.69.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)][B(C_6F_5)_4]$ (9b). A solution of $(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)Cl$ (1.93 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlB(C_6F_5)_4$ (2.21 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlCl was removed by filtration. The solution was cooled to −78 °C to give yellow knots, which were isolated as described above: yield 1.66 g (47%). ESIpos-MS (CH_2Cl_2): *m/e* 733 ($[\{(C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)]^+$), 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$). For NMR data, see Tables 1 and S2. Anal. Calcd for $C_{30}H_{64}ClP_2Pd_2{\cdot}C_{24}BF_{20}$ (1414.1): C, 45.87; H, 4.56; P, 4.38; Pd, 15.05. Found: C, 45.50; H, 4.46; P, 4.19; Pd, 14.42.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$ (9c). A solution of $(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)Cl$ (1.93 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlB\{3,5\text{-}C_6H_3(CF_3)_2\}_4$ (2.67 g, 2.50 mmol) at −30 °C for 1 h. After removal of the TlCl an equal volume of pentane was added. The solution was cooled to −78 °C to give a yellow precipitate, which was isolated as described above: yield 3.56 g (89%). ESIpos-MS (CH_2Cl_2): *m/e* 733 ($[\{(C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)]^+$), 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$). For NMR data, see Table S2. Anal. Calcd for $C_{30}H_{64}ClP_2Pd_2{\cdot}C_{32}H_{12}BF_{24}$ (1598.3): C, 46.59; H, 4.79; B, 0.68; Cl, 2.22; P, 3.88; Pd, 13.32. Found: C, 46.68; H, 5.22; B, 0.65; Cl, 2.17; P, 3.70; Pd, 12.68.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)][Al\{OC(CF_3)_3\}_4]$ (9d). A yellow solution of $(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)Cl$ (1.93 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $LiAl\{OC(CF_3)_3\}_4$ (2.44 g, 2.50 mmol) at −30 °C for 1 h. After removal of the precipitated LiCl an equal volume of pentane was added. Cooling the solution to −78 °C gave a yellow precipitate, which was isolated as described above: yield 3.23 g (76%). ESIpos-MS (CH_2Cl_2): *m/e* 733 ($[\{(C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Cl)]^+$), 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$). For NMR data, see Table S2. $C_{30}H_{64}ClP_2Pd_2{\cdot}C_{16}AlF_{36}O_4$ (1702.2).

$[\{(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Br)][OTf]{\cdot}0.5THF$ (10a). Route a. A yellow solution of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Br$ (775 mg, 2.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid TlOTf (354 mg, 1.00 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration (−30 °C), the solvent was evaporated, and the oily residue was dissolved in 10 mL of THF. After addition of an equal volume of diethyl ether off-white microcrystals separated at −60 °C. The crystals were washed with a small volume of cold ether (−78 °C) and dried under vacuum (20 °C): yield 725 mg (82%).

Route b. The solution of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Br$ (194 mg, 0.50 mmol) in 6 mL of THF was combined with a suspension of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)OTf$[16] (228 mg, 0.50 mmol) in 15 mL of diethyl ether at ambient temperature. The resulting yellow-greenish solution was cooled to −78 °C to give off-white microcrystals: yield 310 mg (70%). ESIpos-MS (CH_2Cl_2): *m/e* 693 ($[\{(C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Br)]^+$, 100), 307 ($[(C_3H_5)Pd(P^iPr_3)]^+$, 50). For NMR data, see Table S2. Anal. Calcd for $C_{24}H_{52}BrP_2Pd_2{\cdot}CF_3O_3S{\cdot}C_2H_4O_{0.5}$ (880.5): C, 36.83; H, 6.41; Br, 9.07; F, 6.47; O, 6.36; P, 7.04; Pd, 24.17; S, 3.64. Found: Br, 9.25; P, 7.31; Pd, 24.17.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Br)][B(C_6F_5)_4]$ (10b). A yellow solution of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Br$ (775 mg, 2.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlB(C_6F_5)_4$ (883 mg, 1.00 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration, and the solvent was completely evaporated under vacuum to leave an off-white analytically pure fibrous solid: yield 1230 mg (89%). ESIpos-MS (CH_2Cl_2): *m/e* 693 ($[\{(C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Br)]^+$, 50), 307 ($[(C_3H_5)Pd(P^iPr_3)]^+$, 100). For NMR data, see Tables 1 and S2. The product dissolves very well in THF and diethyl ether, but not in pentane and could not be crystallized from its solutions. Anal. Calcd for $C_{24}H_{52}BrP_2Pd_2{\cdot}C_{24}BF_{20}$ (1374.4): C, 41.95; H, 3.81; B, 0.79; Br, 5.81; F, 27.65; P, 4.51; Pd, 15.49. Found: C, 41.92; H, 3.74; Br, 5.85; P, 4.44; Pd, 15.31.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Br)][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$ (10c). An orange solution of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Br$ (1.94 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlB\{3,5\text{-}C_6H_3(CF_3)_2\}_4$ (2.67 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration. The solution was cooled below −78 °C to give an orange-yellow precipitate, which was freed from the mother liquor by cannulation, washed with a small volume of cold pentane (−78 °C), and dried under vacuum (−30 °C): yield 0.90 g (23%). For NMR data, see Table S2. $C_{24}H_{52}BrP_2Pd_2{\cdot}C_{32}H_{12}BF_{24}$ (1558.6). Although the compound formed only a powder, it was NMR spectroscopically pure.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)\}_2(\mu\text{-}Br)][Al\{OC(CF_3)_3\}_4]$ (10d). An orange solution of $(\eta^3\text{-}C_3H_5)Pd(P^iPr_3)Br$ (1.94 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $LiAl\{OC(CF_3)_3\}_4$ (2.44 g, 2.50 mmol) at −30 °C for 1 h. The off-white precipitate of LiBr was removed by filtration, and the solution was concentrated in a vacuum to half the volume. Cooling the solution to −78 °C gave an orange precipitate, which was isolated as described above: yield 1.95 g (47%). For NMR data, see Table S2. Anal. Calcd for $C_{24}H_{52}BrP_2Pd_2{\cdot}C_{16}AlF_{36}O_4$ (1662.5): C, 28.90; H, 3.15; Al, 1.62; Br, 4.81; F, 41.14; O, 3.85; P, 3.73; Pd, 12.80. Found: C, 29.12; H, 3.35; Al, 1.85; Br, 5.26; P, 4.10; Pd, 13.86.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)][OTf]$ (11a). A yellow solution of $(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)Br$ (2.15 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid TlOTf (0.88 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration (−30 °C). Evaporation of the solvent under vacuum went along with foaming. The residue was redissolved in 5 mL of THF (−20 °C), and about twice the volume of diethyl ether was added until the solution became turbid. Cooling the solution to −78 °C gave yellow crystals, which were freed from the mother liquor by cannulation, washed with a small volume of cold ether (−78 °C), and dried under vacuum (−30 °C): yield 1.65 g (71%). ESIpos-MS (CH_2Cl_2): *m/e* 777 ($[\{(C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)]^+$), 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$). For NMR data, see Table S2. Anal. Calcd for $C_{30}H_{64}BrP_2Pd_2{\cdot}CF_3O_3S$ (928.6): C, 40.10; H, 6.95; Br, 8.60; F, 6.14; O, 5.17; P, 6.67; S, 3.45; Pd, 22.92. Found: C, 39.82; H, 6.75; Br, 8.46; P, 6.59; Pd, 22.92.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)][B(C_6F_5)_4]$ (11b). A yellow solution of $(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)Br$ (2.15 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlB(C_6F_5)_4$ (2.21 g, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration at −30 °C. About an equal volume of diethyl ether was added until the solution became turbid. Cooling to −78 °C afforded yellow cubes, which were isolated as described above: yield 3.17 g (87%). ESIpos-MS (CH_2Cl_2):

m/e 777 ($[\{(C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)]^+$), 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$). For NMR data, see Tables 1 and S2. Anal. Calcd for $C_{30}H_{64}BrP_2Pd_2{\cdot}C_{24}BF_{20}$ (1458.5): C, 44.47; H, 4.42; B, 0.74; Br, 5.48; F, 26.05; P, 4.25; Pd, 14.59. Found: C, 44.65; H, 4.38; Br, 5.73; P, 4.42; Pd, 15.42.

X-ray Crystal Structure Analysis of 11b. Crystal data: $[C_{30}H_{64}BrP_2Pd_2][BC_{24}F_{20}]$, pale yellow cubes from dichloromethane, $M_r = 1458.51$, crystal size $0.10 \times 0.22 \times 0.26$ mm, $a = 14.8137(1)$ Å, $b = 22.6355(1)$ Å, $c = 17.6457(1)$ Å, $\beta = 103.9953(3)°$, $V = 5741.2(1)$ Å^3, $T = 100$ K, monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$, $d_{calcd} = 1.687$ g cm^{-3}, $F(000) = 2920$, Nonius KappaCCD diffractometer, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.48$ mm^{-1}, 150 322 measured and 18 299 independent reflections ($R_{int} = 0.050$), 15 872 with $I > 2\sigma(I)$, $\theta_{max} = 31.03°$, $T_{min} = 0.758$, $T_{max} = 0.862$, direct methods (*SHELXS-97*) and least-squares refinement (*SHELXl-97*) on F_o^2, both programs from G. Sheldrick, University of Göttingen, 1997; 747 parameters. The meso atoms of the η^3-allyl groups attached to Pd are disordered over two positions (50:50) and two C atoms of one tri-*tert*-butylphosphine ligand show signs of disorder (70:30). H atoms on major component riding, Chebyshev weights, $R_1 = 0.0484$ ($I > 2\sigma(I)$), $wR_2 = 0.1239$ (all data), $\Delta\rho_{max/min} = 3.747/\text{-}4.405$ e Å^{-3} (0.64/0.67 Å from Pd1).

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$ (11c). A yellow solution of (η^3-C_3H_5)Pd(P^tBu_3)Br (2.15 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlB\{3,5\text{-}C_6H_3(CF_3)_2\}_4$ (2.67 g, 2.50 mmol) at −30 °C for 1 h. The precipitated TlBr was removed by filtration and the solution was concentrated to half the volume. Cooling the solution to −78 °C gave orange-yellow knots, which were isolated as described and dried under vacuum (−30 °C): yield 2.30 g (56%). ESIpos-MS (CH_2Cl_2): *m/e* (%) 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$, 100). For NMR data, see Table S2. Anal. Calcd for $C_{30}H_{64}BrP_2Pd_2{\cdot}C_{32}H_{12}BF_{24}$ (1642.8): C, 45.33; H, 4.66; B, 0.66; Br, 4.86; P, 3.77; Pd, 12.96. Found: C, 45.26; H, 4.88; B, 0.64; Br, 4.69; P, 3.61; Pd, 12.63.

$[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)][Al\{OC(CF_3)_3\}_4]$ (11d). A yellow solution of (η^3-C_3H_5)Pd(P^tBu_3)Br (2.15 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $LiAl\{OC(CF_3)_3\}_4$ (2.44 g, 2.50 mmol) at −30 °C for 1 h. The precipitated TlBr was removed by filtration, and the solution was concentrated to about 10 mL. Cooling the solution to −78 °C gave a yellow precipitate, which was isolated as described above: yield 2.40 g (62%). ESIpos-MS (CH_2Cl_2): *m/e* 777 ($[\{(C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)]^+$), 349 ($[(C_3H_5)Pd(P^tBu_3)]^+$). For NMR data, see Table S2. Anal. Calcd for $C_{30}H_{64}BrP_2Pd_2{\cdot}C_{16}AlF_{36}O_4$ (1746.6): C, 31.63; H, 3.69; Al, 1.54; Br, 4.57; F, 39.16; O, 3.66; P, 3.55; Pd, 12.19. Found: C, 31.87; H, 3.50; P, 3.65; Pd, 12.48.

Reaction of (η^3-C_3H_5)Ni(PMe_3)Br with $TlPF_6$: $[(\eta^3\text{-}C_3H_5)Ni(PMe_3)_2][PF_6]$ (12). A deep red solution of (η^3-C_3H_5)Ni(PMe_3)Br (1.28 g, 5.00 mmol) in 15 mL of CH_2Cl_2 was stirred with solid $TlPF_6$ (880 mg, 2.50 mmol) at −30 °C for 1 h. The light yellow precipitate of TlBr was removed by filtration. Cooling the solution to −78 °C gave an orange precipitate, which was isolated as described above: yield 640 mg (32% relating to Pd). ESIpos-MS (CH_2Cl_2): *m/e* 251 ($[(C_3H_5)Ni(PMe_3)_2]^+$, 100). ^{1}H NMR: δ ~5.3 (m, 1H, H_{meso}), 4.00 (m, 2H, H_{syn}), 2.66 (m, 2H, H_{anti}), 1.50 (m, 18H, Me). ^{13}C NMR: δ 116.2 (1C, C_{meso}), 67.8 (2C, C_{term}), 16.6 (6C, Me). ^{31}P NMR: δ −13.8. $C_9H_{23}F_6NiP_3$ (396.9).

Reaction of (η^3-C_3H_5)Pd(PMe_3)Cl with $TlPF_6$: $[(\eta^3\text{-}C_3H_5)Pd(PMe_3)_2][PF_6]$ (13). Synthesis was as described above, but reacting a yellow solution of (η^3-C_3H_5)Pd(PMe_3)Cl (1.295 g, 5.00 mmol) with $TlPF_6$ (880 mg, 2.50 mmol) to afford a light yellow precipitate: yield 670 mg (30% relating to Pd). ESIpos-MS (CH_2Cl_2): *m/e* 299 ($[(C_3H_5)Pd(PMe_3)_2]^+$, 100). ^{1}H NMR: δ 5.51 (m, 1H, H_{meso}), 4.32 (m, 2H, H_{syn}), 3.12 (m, 2H, H_{anti}), 1.59 (m, 18H, Me). ^{13}C NMR: δ 122.8 (1C, C_{meso}), 70.4 (2C, C_{term}), 17.6 (6C, Me). ^{31}P NMR: δ −18.7. $C_9H_{23}F_6P_3Pd$ (444.6).

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Supporting Information Available: Supplementary NMR data (Tables S1 and S2) and tables of X-ray data collection information, atom coordinates and thermal parameters, and bond lengths and angles (Tables S3−S10 and Figures S1 and S2), together with CIF data, for **6c** and **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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