Structural and ^{13}C NMR Studies on Palladium MOP Compounds: A New Weak C−Pd σ-Bond Plus MOP as a Bridging Diene Ligand

Pascal Dotta, P. G. Anil Kumar, and Paul S. Pregosin*

Laboratory of Inorganic Chemistry, ETHZ, 8093 Zürich, Switzerland

Alberto Albinati* and Silvia Rizzato

Department of Structural Chemistry (DCSSI and the Faculty of Pharmacy), University of Milan, 20133 Milan, Italy

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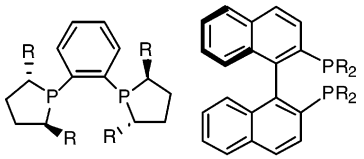
A new set of Pd-MOP complexes (MOP = (*S*)-2-diarylphosphino-1,1′-binaphthyl) has been prepared. One of these, containing MeO-MOP (=2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl), is shown to act as a chelating ligand with a naphthyl backbone diene bridging a Pd(I)−Pd(I) bond. This bonding mode exists in both the solid and solution states. A series of chloro-Pd(II)MOP complexes containing the well-known cyclometalated *N*,*N*-dimethyl benzylamine chelate have been treated with NaBArF to extract the chloride ligand. The products, starting from the H-MOP, MeO-MOP, and NC-MOP analogues, are all different. Of particular interest is the product from the H-MOP reaction in that the fourth coordination position is occupied by a weak Pd−C σ-bond from the naphthyl backbone, on the basis of ^{13}C NMR data. The rate of product formation in the Pd-catalyzed hydrosilylation of styrene with $SiHCl_3$ has been measured as a function of time for the four auxiliaries H-MOP, MeO-MOP, HO-MOP, and NC-MOP. The NC-MOP is shown to be much faster than the others, and a tentative explanation is offered.

Introduction

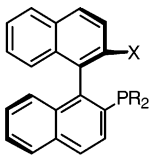
Enantioselective homogeneous catalysis employing late transition metal complexes represents a research area of growing interest[1−5] Relatively small quantities of complexed chiral auxiliaries, be they oxazolines[4] or phosphines,[1,3,5] can be used to prepare substantial amounts of optically pure organic compounds. Although much interest has centered on Ru(II)- or Rh(I)-catalyzed enantioselective hydrogenation, palladium-catalyzed carbon−carbon (and carbon−nitrogen[4] and carbon−oxygen, etc.) bond making reactions are increasingly popular.[2−7]

Frequently, chiral catalysts employ tertiary phosphine derivatives as auxiliaries. Indeed, bidentate chiral phosphines have become so popular that these are increasingly commercially available, e.g., Duphos and Binap. However, the recent literature shows that much



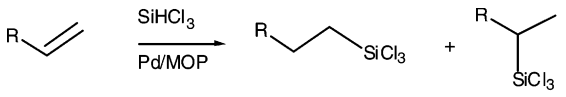
Duphos Binap

effort is being invested in the applications of *monodentate* chiral auxiliaries, e.g., MOP, **1**.[8−14] The ligands **1**



1a, X = H; **1b,** X = OMe; **1c,** X = OH; **1d,** X = CN; R = Ph

are good auxiliaries for the Pd-catalyzed regioselective and enantioselective hydrosilylation reaction,[8] eq 1, with the branched product being favored.



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(1) Burk, M. J.; Cross, M. F.; Martinez, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 9375. Burk, M. J. *Acc. Chem. Res.* **2000**, *33*, 363−372.
(2) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336−345.
(3) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48−58.
(4) Zim, D.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2413−2415. Anderson, K. W.; Mendez-Perez, M.; Priego, J.; Buchwald, S. L. *J. Org. Chem.* **2003**, *68*, 9563−9573. Huang, X. H.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J Am. Chem Soc.* **2003**, *125*, 10767−10767. Muci, A. R.; Buchwald, S. L. *Cross-Coupling Reactions* **2002**, *219*, 131−209. Alcazar-Roman, L. M.; Culkin, D. A.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234−245. Hartwig, J. F.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *J Am. Chem Soc.* **2000**, *122*, 4618−4630. Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 3694−3703. Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, 1998.
(5) Tye, H. *J. Chem. Soc., Perkin Trans. 1* **2000**, 275−298. Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron Asymmetry* **1998**, *9*, 1−45.
(6) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. Trost, B. M.; Rasdinov, R.; Grenzer, E. M. *J. Am. Chem. Soc.* **1997**, *119*, 7879−7880.
(7) van Leeuwen, P.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741−2769.

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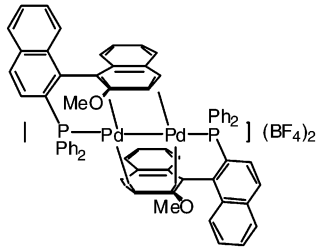
Although the structural coordination chemistry associated with chiral bidentate phosphine auxiliaries has been well studied, there is relatively little literature on the structural transition metal chemistry associated with **1**. Further, that which is known with respect to the interactions of **1** with Pd(II) affords a rather mixed picture. Scheme 1 shows a few of the complexes, **2**−**6** and **8** (from **7**), that have been characterized and reveals that a number of binding modes are possible.

The MOP ligand can function as a σ-donor in complexes **3**, **4**, and **6** (i.e., as a P,C bidentate), but as a phosphine, π-olefin chelate in compounds **2**, **5**, and **8**. Further, more than one naphthyl double bond can be involved. ^{13}C NMR studies have confirmed the diene nature of **2**.[13] Although **2** has not been crystallized, both NMR and X-ray crystallography support the proposed structures of **3**,[14] **4**,[14] **5**,[12c] **6**,[9a,12c] and **8**.[15] Complex **3** arises when ligand **1c** adopts an ene-one anionic structure. Complex **4**, with its rather long σ-bond, ca. 2.19 Å,[14] has the positive charge in the cation localized in the organic backbone. It would seem that it is not easy to predict how the MOP-type ligands will bind to Pd(II) since both σ- and π-bonds can be formed using different parts of the aryl backbones (e.g., to carbons 1 and 6 in **8**, but to the immediately adjacent double bond in **5**). In any case, **1** and related MOP-type ligands seem to be capable of acting as multidentate ligands.[16] We report here new Pd-MOP complexes in which there are further subtle variations on the bonding from the naphthyl backbone.

Results and Discussion

Dinuclear Pd(I) Compound 9. During the preparation of the acetylacetonate compound **4**, a modest quantity of a new dinuclear Pd(I) species was obtained as a side-product and its structure determined via X-ray diffraction. Once the structure was known, the new dinuclear complex, **9**, could be prepared in good yield by direct reaction of the known Pd(I) dimer $[Pd_2(CH_3CN)_6](BF_4)_2$ with 2 equiv of MeO-MOP, as shown in the eq 2:

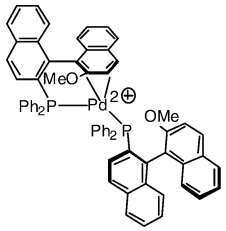
$$[Pd_2(CH_3CN)_6](BF_4)_2 \xrightarrow{2\ \text{MeO-MOP}} \mathbf{9} \qquad (2)$$



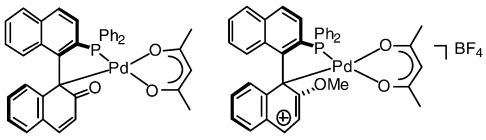
9

In this complex, the naphthyl backbone of **1b** acts as a bridging diene ligand. The ^{13}C data for **9** (see Figure 1 and Table 1 for data and numbering) show that the two fully substituted carbons, 1 (99.7 ppm) and 6 (136.7 ppm), and the two =CH carbons 4 (85.0 ppm) and 5 (79.4 ppm) show typical strongly low-frequency-shifted signals, due to the π-complexation.

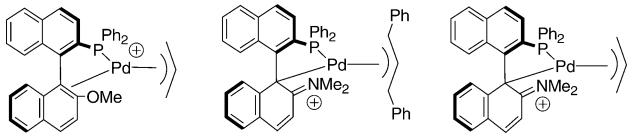
Scheme 1. MOP Complexes Showing Novel Interactions



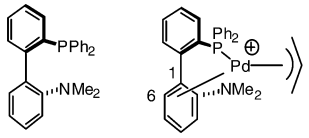
2[13]



3[14] **4**[14]



5[12c] **6a**[9a] **6b**[12c]



7 **8**[15]

(8) (a) Uozumi, Y.; Kitayama, K.; Hayashi, T. *Tetrahedron Asymmetry* **1993**, *4*, 2419−2422. (b) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775−776. (c) Uozumi, Y.; Kitayama, K.; Hayashi, T.; Kazunori, K.; Yanagi, K.; Fukuyo, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713−722. (d) Hayashi, T. *Acta Chem. Scand.* **1996**, *50*, 259−266. (e) Uozumi, Y.; Danjo, H.; Hayashi, T. *Tetrahedron Lett.* **1998**, *39*, 8303−8306. (f) Uozumi, Y. *Yakugaku Zasshi-J. Pharm. Soc. Jpn.* **1998**, *118*, 193−205. (g) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681−1687. (h) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354−362. (i) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y. *Chem. Lett.* **2000**, 1272−1273. (j) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y. *J. Org. Chem.* **2001**, *66*, 1441−1449. (k) Hayashi, T.; Han, J. S.; Takeda, A.; Tang, J.; Nohmi, K.; Mukaide, K.; Tsuji, H.; Uozumi, Y. *Adv. Synth. Catal.* **2001**, *343*, 279−283. (l) Shimada, T.; Mukaide, K.; Shinohara, A.; Han, J. W.; Hayashi, T. *J Am. Chem Soc.* **2002**, *124*, 1584−1585.

(9) (a) Wang, X. P.; Li, X.; Sun, J.; Ding, K. *Organometallics* **2003**, *22*, 1856−1862. (b) Xu, L.; Shi, Q.; Li, X.; Jia, X.; Huang, X.; Wang, R.; Zhou, Z.; Lin, Z.; Chan, A. S. C. *Chem. Commun.* **2003**, 1666−1667.

(10) Soleilhavoup, M.; Viau, L.; Commenges, G.; Lepetit, C.; Chauvin, R. *Eur. J. Inorg. Chem.* **2003**, 207−212.

(11) Maillard, D.; Bayardon, J.; Kurichiparambil, J. D.; Nguefack-Fournier, C.; Sinou, D. *Tetrahedron: Asymmetry* **2002**, *13*, 1449−1456.

(12) (a) Gouriou, L.; Lloyd-Jones, G. C.; Vyskocil, T.; Kocovsky, P. *J. Organomet. Chem.* **2003**, *687*, 525−537. (b) Lloyd-Jones, G. C.; Stephen, S. C.; Murray, M.; Butts, C. P.; Vyskocil, S.; Kocovsky, P. *Chem. Eur. J.* **2000**, *6*, 4348−4357. (c) Kocovsky, P.; Vyskocil, S.; Cisarova, I.; Sejbal, J.; Tislerova, I.; Smrcina, M.; Lloyd-Jones, G. C.; Stephen, S. C.; Butts, C. P.; Murray, M.; Langer, V. *J. Am. Chem. Soc.* **1999**, *121*, 7714−7715.

(13) Dotta, P.; Kumar, P. G. A.; Pregosin, P. S.; Albinati, A. *Helv. Chim. Acta* **2004**, *87*, 272−278.

(14) Dotta, P.; Kumar, P. G. A.; Pregosin, P. S.; Albinati, A.; Rizzato, S. *Organometallics* **2003**, *22*, 5345−5349.

(15) Faller, J. W.; Sarantopoulos, N. *Oranometallics* **2004**, *23*, 2008−2014.

(16) There are now a few examples involving Pd(0), see: Marshall, W. J.; Grushin, V. V. *Organomertallics* **2003**, *22*, 555−562. Yin, J. J.; Rainka, M. P.; Zhang, X. X.; Buchwald, S. L. *J Am. Chem Soc.* **2002**, *124*, 1162−1163. Reid, S. M.; Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7816−7817.

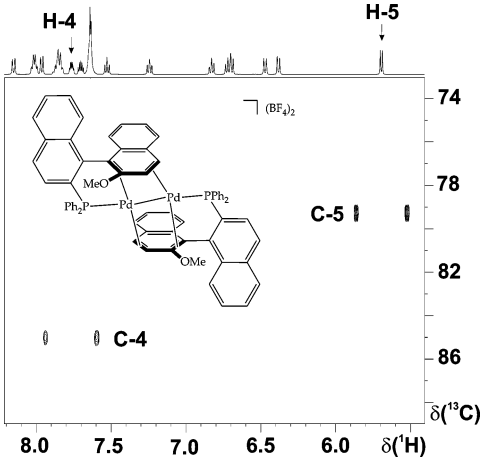
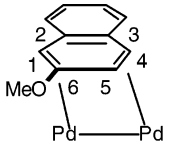


Figure 1. Section of the ^{13}C HMQC spectrum for **9**, showing the cross-peaks for the two coordinated ═CH resonances, at relatively low frequency.

Table 1. ^{13}C Chemical Shifts and $\Delta\delta$ Values[a] for 9 and MeO-MOP



carbon	MeO-MOP	**9**	$\Delta\delta$
1	122.0	99.7	−22.3
2	134.4	131.6	−2.8
3	129.1	123.4	−5.7
4	130.2	85.0	−45.2
5	113.0	79.4	−33.6
6	155.5	136.7	−18.8
OMe	55.7	57.6	+1.9

[a] 500 MHz, CD_2Cl_2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 9[a]

Pd(1)−Pd(2)	2.7265(4)	Pd(2)−P(2)	2.305(1)
Pd(1)−P(1)	2.313(1)	Pd(2)−C(2B)	2.626(4)
Pd(1)−C(10A)	2.388(3)	Pd(2)−C(10B)	2.495(4)
Pd(1)−C(8B)	2.181(4)	Pd(2)−C(8A)	2.212(4)
Pd(1)−C(9B)	2.336(4)	Pd(2)−C(9A)	2.260(5)
Pd(1)−C(1A)	2.171(4)	Pd(2)−C(1B)	2.182(4)
C(1A)−C(2A)	1.491(7)	C(1B)−C(2B)	1.493(6)
C(1A)−C(11A)	1.493(6)	C(1B)−C(11B)	1.512(7)
C(1A)−C(10A)	1.423(6)	C(1B)−C(10B)	1.409(8)
C(2A)−C(7A)	1.416(6)	C(2B)−C(7B)	1.412(6)
C(7A)−C(8A)	1.423(7)	C(7B)−C(8B)	1.427(7)
C(8A)−C(9A)	1.390(7)	C(8B)−C(9B)	1.405(6)
C(9A)−C(10A)	1.423(6)	C(9B)−C(10B)	1.414(6)
P(1)−Pd(1)−Pd(2)	173.31(3)	P(2)−Pd(2)−Pd(1)	175.35(3)

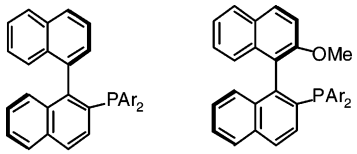
[a] The numbering scheme used in this table differs from that used for the NMR due to the need to distinguish the two halves (rings a and b) of the MeO-MOP ligand.

Suitable crystals of **9** were obtained from dichloromethane/pentane, and a view of the structure for this dication is shown in Figure 2. A list of selected bond distances and bond angles is given in Table 2. The structure of the complex clearly shows the Pd−Pd bond, with a separation, Pd(1)−Pd(2) = 2.727 Å. This distance is well within the expected range[17] for this type of metal−metal bond. Hayashi and co-workers have reported the solid-state structures for $PdCl(\eta^3\text{-}CH_2C(Me)CH_2)$(MeO-MOP)[8b] and *trans*-$PdCl_2$(MeO-MOP)$_2$,[8c] and the Pd−P distances in these molecules, ca. 2.31 Å and ca. 2.34 Å, respectively, are in good agreement with the two Pd−P separations found in **9**: Pd(2)−P(2) = 2.305(1) Å and Pd(1)−P(1) = 2.313(1) Å. There are eight Pd−(olefin carbon) distances: four from the fully substituted carbons, Pd(1)−C(1A) = 2.171(4) Å, Pd(1)−C(10A) = 2.388(3) Å, Pd(2)−C(1B) = 2.182(4) Å, and Pd(2)−C(10B) = 2.495(4) Å, plus four from the ═CH carbons, Pd(2)−C(8A) = 2.212(4) Å, Pd(2)−C(9A) = 2.260(5) Å, Pd(1)−C(8B) = 2.181(4) Å, and Pd(1)−C(9B) = 2.336(4) Å. On the basis of these bond distances, it appears that the Pd−olefin bonding is very asymmetric. Clearly several of these separations are relatively long, since the literature values for Pd−C(η^2-olefin) complexes are on the order of 2.18 Å.[17]

Further, several of the C−C distances are also rather long, e.g., C(1A)−C(2A) at 1.491(7) Å and C(1B)−C(2B) at 1.493(6) Å, suggesting localized single bonds between these atoms.

There are several structural reports of di (or poly) olefins bridging Pd(I) dimers,[18,19] so that there is precedence for the basic structure for **9**; nevertheless it is noteworthy that the MOP ligand complexes in this fashion.

Cyclometalated Complexes with MOP. Although it is now abundantly clear that the naphthyl backbone in atropisomeric phosphines can be involved in π-bonding to the Pd(II) (and also to Ru(II)[20,21]), the range of bonding types is not yet well defined. To further explore this area, the cyclopalladated MOP complexes **10** and **11** were prepared via the usual bridge-splitting reaction as shown in Scheme 2. The decision for a cyclometalated Pd complex was based on the fact that many catalytic cycles involving palladium (e.g., hydrosilylation or cross-coupling) contain a reactive species with a metal−carbon σ-bond. The ligands **1a′** and **1b′** (both with Ar = 3,5-di-*t*-Bu-phenyl substituents) were used previously[22] in a catalytic study and serve only as additional examples. Extraction of the chloride with NaBArF in



1a′ **1b′**

Ar = 3,5-di-*t*-Bu-Phenyl

dichloromethane afforded the new derivatives **12** and **13**, in which the methoxy oxygen atoms of **1b** and **1b′**

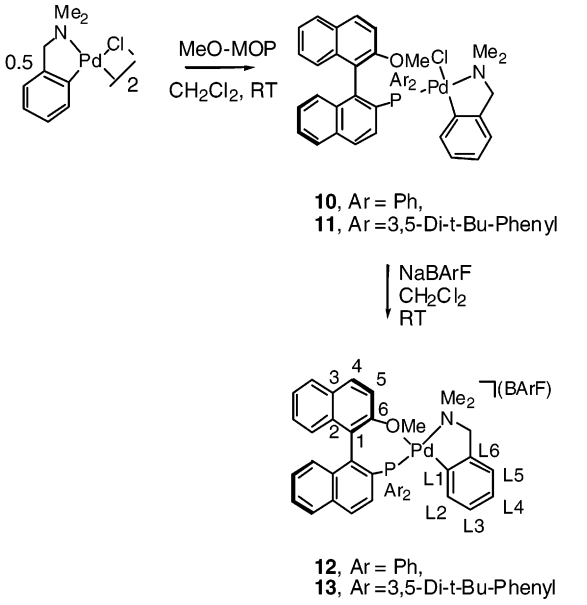
(17) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton* **1989**, S1−S83.

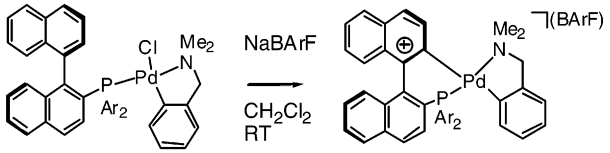
(18) Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1993**, *12*, 4503−4508. Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1996**, *15*, 2047−2052.

(19) Murahashi, T.; Uemura, T.; Kurosawa, H. *J. Am. Chem Soc.* **2003**, *125*, 8436−8437. Murahashi, T.; Okuno, T.; Nagai, T.; Kurosawa, H. *Organometallics* **2002**, *21*, 3679−3682. Murahashi, T.; Otani, T.; Okuno, T.; Kurosawa, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 537. Murahashi, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **1999**, *121*, 10660−10661.

(20) den Reijer, C. J.; Dotta, P.; Pregosin, P. S.; Albinati, A. *Can. J. Chem.* **2001**, *79*, 693−704. Geldbach, T. J.; Pregosin, P. S. *Eur. J. Inorg. Chem.* **2002**, 1907−1918. Geldbach, T. J.; Pregosin, P. S.; Albinati, A. *Organometallics* **2003**, *22*, 1443−1451, and references therein.

Scheme 2. Cyclopalladated Complexes with MeO-MOP and H-MOP





14, Ar = Ph

15, Ar = 3,5-di-*t*-buphenyl

16 Ar = Ph

17, Ar = 3,5-di-*t*-buphenyl

are now complexed to the Pd(II). The geometry shown, which places the MeO and Me_2N groups close to one another, is supported by NOESY results (see Figure 3).

^{13}C NMR results for these new compounds are given in Table 3. We note that, for **12** and **13**, there is a 9.5−10.5 ppm high-frequency shift of the methoxy carbon, relative to **10** and **11**, respectively, due to the oxygen coordination. The cyclopalladated carbon resonance, L1, is shifted ca. 10−11 ppm to low frequency, in agreement with the expectation of a weaker ligand than chloride in *trans* position.[23] The aromatic carbons C1−C6 change minimally relative to the chloride analogue. These NMR data for complexes **10**−**13** are useful primarily as models for the ^{13}C NMR studies, which will follow.

Scheme 2 also shows structures for the cyclopalladated H-MOP complexes, **16** and **17**, derived from the same reactions (bridge splitting to afford **14** and **15** and then chloride extraction). Table 4 shows the pertinent ^{13}C data. The backbone carbon C-1 has now shifted to

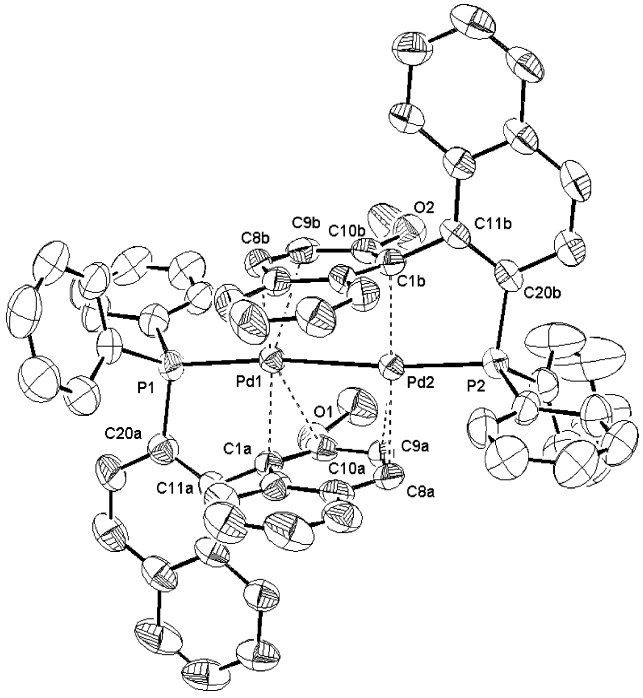


Figure 2. ORTEP view of the structure of complex dication **9**. Ellipsoids are drawn at 50% probability. The numbering scheme used in this figure differs from that used for the NMR, due to the need to distinguish the two halves (rings a and b) of the MeO-MOP ligand.

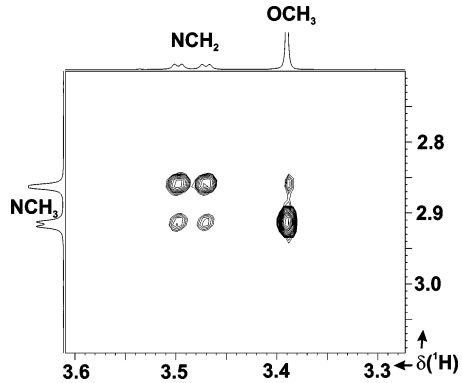


Figure 3. Section of the 2-D NOESY NMR spectrum for **12**, showing the cross-peaks due to the NOEs from the proximate MeO (and NCH_2) groups to the nonequivalent Me_2N groups (on the *y*-axis). One of the *N*-methyl groups is coupled to the MOP ^{31}P atom.

higher frequency (15.8 and 14.1 ppm for **16** and **17**, respectively), while C-6 (which is closer to the Pd atom) has shifted markedly to *lower* frequency (−24.4 and −26.3 ppm for **16** and **17**, respectively). We consider these NMR data to be consistent with some weak σ-bonding character between C-6 and the Pd atom, in analogy with what we have observed in **4**. The much smaller coordination chemical shift for C-6 in **16** and **17** (ca. −25 ppm) relative to **4** (ca. −50 ppm) arises due to the presence of a good σ-donor (the cyclopalladated carbon) rather than the acetyl acetonate oxygen donor in **4**, i.e., differences in *trans* influence effects. We suggest some positive charge at C-1 and thus the high frequency shift, although some of the charge is surely delocalized over the naphthyl fragment. We cannot exclude the possibility of an $\eta^1-\pi$ bond, i.e., an interaction from the π-orbital of a single naphthyl carbon, as

(21) Cyr, C. W.; Rettig, S. J.; Patrick, B. O.; James, B. R. *Organometallics* **2002**, *21*, 4672−4679. Doherty, S.; Newman, C. R.; Hardacre, C.; Nieuwenhuyzen, M.; Knight, J. G. *Oranometallics* **2003**, *22*, 1452−1462.

(22) Dotta, P.; Kumar, P. G. A.; Pregosin, P. S.; Albinati, A.; Rizzato, S. *Organometallics* **2004**, *23*, 2295−2304.

(23) Tschoerner, M.; Kunz, R. W.; Pregosin, P. S. *Magn. Reson. Chem.* **1999**, *37*, 91−97. Tschoerner, M.; Pregosin, P. S. *Inorg. Chim. Acta* **1999**, *290*, 95−99.

Table 3. ^{13}C Chemical Shifts[a] for 10−13

Ar = Ph	**10**	**12**	Δδ
1	119.9	125.2	+5.3
2	134.6	132.7	−1.9
3	129.1	132.2	+3.1
4	130.6	132.8	+2.2
5	112.2	119.5	+7.3
6	154.7	155.5	+0.8
OCH_3	55.3 (3.40[b])	65.8 (3.39[b])	+10.5
L1	151.8	140.9	−10.9
Ar = 3,5-*t*-Bu	**11**	**13**	Δδ
1	121.6	125.4	+3.8
2	134.5	133.2	−1.3
3	128.9	131.9	+3.0
4	130.4	133.0	+2.6
5	113.8	119.5	+5.7
6	155.6	155.2	−0.4
OCH_3	56.3 (3.33[b])	65.8 (3.39[b])	+9.5
L1	151.6	141.6	−10.0

[a] 500 MHz, CD_2Cl_2. [b] ^{1}H chemical shift.

Table 4. ^{13}C Chemical Shifts[a] for 14−17

Ar = Ph	**14**	**16**	Δδ
1	133.4	149.2	+15.8
2	133.0	132.0	−1.0
3	133.3	134.5	+1.2
4	129.2	131.3	+2.1
5	125.0	127.5	+2.5
6	131.0[b]	106.6[c]	−24.4
L1	150.1	149.4	−0.7
Ar = 3,5 *t*-Bu	**15**	**17**	Δδ
1	136.2	150.3	+14.1
2	133.4	132.1	−1.3
3	133.0	134.6	+1.6
4	129.3	131.1	+1.8
5	125.1	127.7	+2.6
6	131.7	105.4	−26.3
L1	150.4	150.4	0.0

[a] 500 MHz, CD_2Cl_2. [b] $^1J_{CH}$(C6) = 163 Hz for **14**. [c] $^1J_{CH}$(C6) = 155 Hz for **16**.

this has been proposed recently;[24] however, an η^1-bond does not usually result in a strong high-frequency shift for the adjacent carbon. In any case, whether the new interaction represents an extremely weak σ-bond or some form of π-polarization, this represents yet another new bonding possibility for Pd-MOP.

The $^1J(^{13}C,^1H)$ values for the hydrogen at C-6 are 163 and 155 Hz for **14** and **16**, respectively, so that we have no reason to consider an agostic interaction. The chemical shift of the cyclopalladated carbon resonance, L1, is more or less unchanged relative to the chloride analogue; that is, the *trans* influence of this new bond is similar to that of a chloride.

The solid-state structure of the chloride complex **15** is known.[22] An ORTEP view of this neutral species is shown as Supplementary Figure 1. Given that carbon C6 is quite close in space to the position occupied by the chloride ligand, it is not difficult to imagine an interaction from this carbon, once the chloride is removed via the NaBArF reagent.

Scheme 3 shows an analogous reaction sequence for **1d**, the cyano-MOP derivative. The product, **19**, gives a singlet in the ^{31}P NMR spectrum, plus a microanalysis

(24) Geldbach, T. J.; Drago, D.; Pregosin, P. S. *J. Organomet. Chem.* **2002**, *643*, 214−222. Reid, S. M.; Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7816−7817.

Scheme 3. Cyclopalladated Complexes with NC-MOP

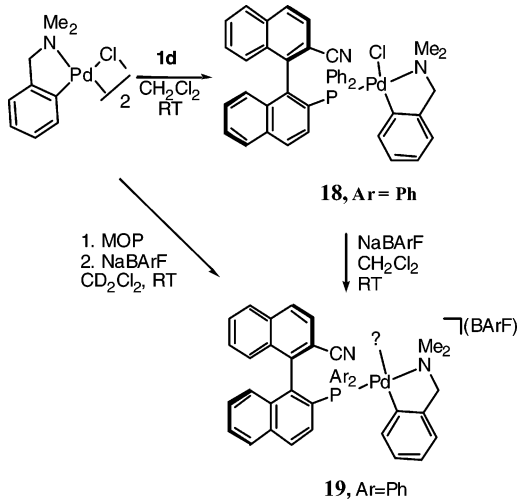


Table 5. ^{13}C Chemical Shifts for 18 and 19[a]

Ar = Ph	**18**	**19**	Δδ
1	142.9	146.2	+3.3
2	133.0	132.0	−1.0
3	134.9	136.0	+1.1
4	129.3	131.6	+2.3
5	127.1	125.2	−1.9
6	112.4	107.3	−5.1
L1	151.9	145.0	−6.9

[a] 500 MHz, CD_2Cl_2.

and a mass spectrum consistent with the formulation [Pd($C_6H_4CH_2NMe_2$)(**1d**)](BArF). The IR spectrum shows a modest 10 cm^{-1} change in the CN frequency on going from **18** to **19**. We find no water signal in either the IR or ^{1}H NMR of **19**. Addition of Bu_4NCl leads to formation of **18** (reverse reaction) cleanly. The ^{13}C data for **19** are given in Table 5 and show that the naphthyl backbone does *not* interact with the metal; that is, there is no evidence for π- or-σ-complexation. Although the exact structure of **19** is not certain (it still might be a dynamic aquo complex, or the nitrile might be involved, weakly, with the Pd(II)), compound **19** does *not show the naphthyl backbone interaction* related to that found for **15** or **17**. We do not believe that **19** is a three-coordinate Pd(II) complex.

In connection with the characterization of the new BArF cations **12**, **16**, and **19**, we note that the electron spray ionization mass spectrum (from methanol) shows a major signal for **19**+MeOH, i.e., the solvated NC-MOP analogue, whereas, the MeO-MOP and H-MOP cations, **12** and **16**, gave strong peaks for the molecular ion, *without solvent*, presumably because the fourth coordination position is blocked as described above.

Comments on Hydrosilylation Catalysis. We have recently noted that NC-MOP, **1d**, seems to produce rather different results than either **1a** or **1b** in terms of its enantioselectivity[22] in the Pd-catalyzed hydrosilylation of styrene (see eq 1). Using 0.05 mol % [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ as precursor, together with 0.2 mol % ligand **1d**, affords the *S* enantiomer, whereas use of **1a**,**b** yields the *R* enantiomer.[22] Further, we have now measured the rate of conversion of styrene as a function of time for the four auxiliaries **1a**−**1d** and show this plot in Figure 4. Clearly, NC-MOP, **1d**, affords a catalyst

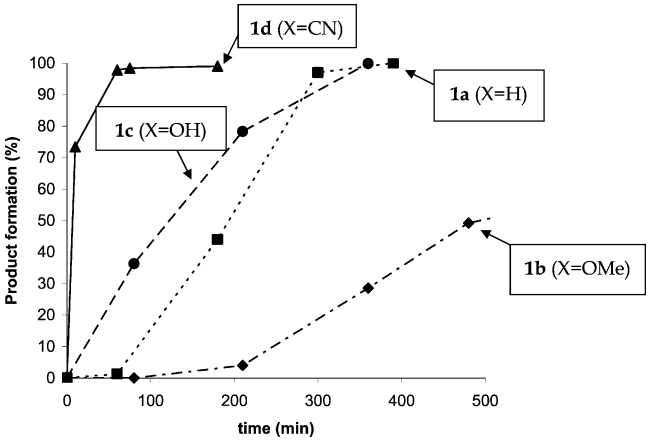


Figure 4. Plot showing the development of product as a function of time for the four auxiliaries, MeO-MOP, H-MOP, OH-MOP, and NC-MOP, in the hydrosilylation of styrene.

that is about 1 order of magnitude faster than the others. Although the reaction is quantitative for all four auxiliaries, there appears to be an incubation period for the H-MOP and MeO-MOP reactions. Interestingly, the observed ee does not follow the kinetics, i.e., 92%, 7%, and 42% for the H, MeO, and CN analogues, respectively.[22]

This difference in kinetic behavior might involve a "simple" electronic effect, based on the differences in the electronic and steric characteristics of the substituents in these ligands.[25] However, given the different ways in which these MOP ligands choose to "occupy" a vacant palladium coordination position (i.e., using the MeO group as oxygen donor from MeO-MOP, or the π-system from the naphthyl backbone of H-MOP, or neither of these, as in the NC-MOP), we suggest that the Pd complexes, which arise from these ligands, may well adopt very different structures along the hyrosilylation reaction pathway. This implies that the choice of MOP ligand, for any given catalytic reaction, is not trivial.

While it is useful to know if the R substituents (and/or the naphthyl backbone) play a role in relevant MOP organometallic chemistry, it may be that chelation, be it via the methoxy oxygen or the naphthyl backbone, only serves to slow one or more of the critical steps (e.g., olefin complexation). However, when the sense of the enantioselectivity is affected, the role of the R substituent becomes important.

Experimental Section

All water- or air-sensitive manipulations were carried out under a nitrogen atmosphere. Pentane and ether were distilled from NaK, THF and toluene from potassium, and CH_2Cl_2 from CaH_2. The MOP ligands,[8] the *N*,*N*′-dimethylbenzylamine cyclopalladated starting material,[26] and the dinuclear compound $[Pd_2(CH_3CN)_6](BF_4)_2$[27] were prepared by literature methods. NMR spectra were recorded with Bruker DPX-250, 300, 400, and 500 MHz spectrometers at room temperature unless otherwise noted. Chemical shifts are given in ppm; coupling constants (*J*) in Hz. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

The numbering system used for the MOP ligands in the NMR measurements is the same as that used previously.[13,14]

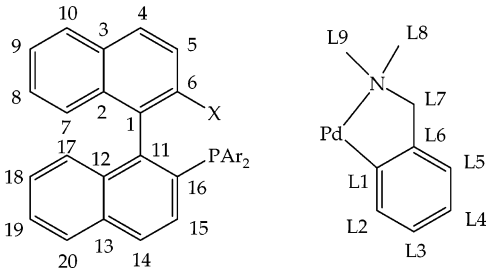


Table 6. Experimental Data for the X-ray Diffraction Study of Compound 9.

formula	$C_{66}H_{50}B_2F_8O_2P_2Pd_2$
mol wt	1323.42
data coll. *T*, K	293
diffractometer	Bruker SMART CCD
cryst syst	monoclinic
space group (no.)	$P2_1$ (4)
a, Å	11.342(1)
b, Å	16.995(1)
c, Å	15.126(3)
β, deg	100.175(2)
V, Å^3	2869.7(4)
Z	2
$\rho_{(calcd)}$, g cm^{-3}	1.532
μ, cm^{-1}	7.54
radiation	Mo Kα (graphite monochrom., $\lambda = 0.71073$ Å)
θ range, deg	$2.18 < \theta < 25.62$
no. data collected	23 404
no. indep data	10 096
no. obsd reflns (n_o) $[\|F_o\|^2 > 2.0\sigma(\|F\|^2)]$	9093
no. of params refined (n_v)	729
abs structure (Flack's) param	0.03(2)
R_{int} [a]	0.0417
R^2 (obs reflns)	0.0336
R_w^2 (obs reflns)[b]	0.0833
GOF[c]	1.026

[a] $R = \sum(|F_o - (1/k)F_c|)/\sum|F_o|$. [b] $R_w^2 = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w|F_o^2|^2]$. [c] GOF $= [\sum w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

Crystallography. Orange crystals of **9**, suitable for X-ray diffraction, were obtained from a dichloromethane/pentane solution and are air stable. A prismatic crystal was mounted on a Bruker SMART diffractometer, equipped with a CCD detector, for the unit cell determination and the data collection. The space group was unambiguously determined from the systematic absences, while the cell constants were refined by least-squares, at the end of the data collection, by using 993 reflections ($\theta_{max} \leq 25.3°$). The data were collected by using ω scans, in steps of 0.3 deg. For each of the 1860 collected frames, counting time was 30 s. Selected crystallographic and other relevant data are listed in Table 6 and in the Supporting Information (Table S1).

Data were corrected for Lorentz and polarization factors with the data reduction software SAINT[27] and empirically for absorption using the SADABS program.[28] The structures were solved by direct and Fourier methods and refined by full matrix least-squares[29] (the function minimized being $\sum[w(F^2_o - (1/k)F^2_c)^2]$). Anisotropic displacement parameters were used for all atoms. The contribution of the hydrogen atoms, in their

(25) The significant difference in rate between the OH and MeO analogues makes a Hammett-type correlation unlikely.
(26) Cope, A. C.; Friedrih, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
(27) *BrukerAXS, SAINT*, Integration Software; Bruker Analytical X-ray Systems: Madison, WI, 1995.
(28) Sheldrick, G. M. *SADABS*, Program for Absorption Correction; University of Göttingen: Göttingen, Germany, 1996.
(29) Sheldrick, G. M. *SHELX-97. Structure Solution and Refinement Package*; Universität Göttingen, 1997.

calculated positions (C−H = 0.95 Å, B(H) = 1.3/1.5B(C_{bonded}) (Å^2)), was included in the refinement using a riding model.

Upon convergence (see Table S1), the final Fourier difference map showed no significant peaks. No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[30] The standard deviations on intensities were calculated in terms of statistics alone. Refining the Flack's parameter tested the handedness of the structure (cf. Table 6).[31] All calculations were carried out by using the PC versions of the SHELX-97[29]and ORTEP programs.[32]

Syntheses. The syntheses of the complexes **10**, **12**, and **16** gave products that contained very small (ca. 1%) quantities of phosphine oxide.

Synthesis of [Pd(1b)]$_2$(BF$_4$), 9. To a mixture of 20 mg of [$Pd_2(CH_3CN)_6$](BF$_4$)$_2$[33] (0.032 mmol) and 29.6 mg of **1b** (0.063 mmol) was added 1.5 mL of CH_3CN and the red solution stirred for 20 min. After removal of the solvent, the residue was precipitated from a CH_2Cl_2/ether solution and washed twice with ether. Recrystallization from CH_2Cl_2/ether gave 20 mg (47%) of **9** as a red crystalline material. Anal. Calcd for $C_{66}H_{50}O_2B_2F_8P_2Pd_2{\cdot}C_2H_4Cl_2$: C, 57.37; H, 3.83. Found: C, 57.32; H, 4.86. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.15 (d, $^3J_{HH}$ = 8.7, *H-14*), 8.01 (m, *Phenyl-H*, 2 H), 7.82−7.89 (m, *Phenyl-H*, 3 H), 7.70 (m, *H-15*), 7.76 (m, *H-4*), 7.60−7.67 (m, *Phenyl-H*, 5 H), 7.53 (dt, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 0.8, *H-19*), 7.24 (dt, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.0, *H-18*), 6.83 (dt, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.1, H-8), 6.72 (t, $^3J_{HH}$ = 7.9, *H-9*), 6.69 (d, $^3J_{HH}$ = 8.4, *H-7*), 6.48 (d, $^3J_{HH}$ = 8.7, *H-17*), 6.39 (d, $^3J_{HH}$ = 8.1, *H-10*), 5.69 (d, $^3J_{HH}$ = 7.2, *H-5*), 3.16 (s, OC*H*$_3$, 3 H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 142.3 (*C-11*), 139.4 (*C-16*), 136.7 (*C-6*), 136.6 (*C-13*), 133.2 (*C-14*), 132.5 (*C-8*), 131.8 (*C-12*), 131.6 (*C-2*), 129.9 (*C-18*), 129.9 (*C-9*), 129.0 (*C-20*), 127.9 (*C-15*), 127.2 (*C-10*), 126.0 (*C-7*), 125.2 (*C-17*), 123.4 (*C-3*), 99.7 (*C-1*), 85.0 (*C-4*), 79.4 (*C-5*), 57.6 (O*C*H$_3$). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 38.4 (s).

Synthesis of PdCl(C$_6$H$_4$CH$_2$NMe$_2$)(1b), 10. To a mixture of 88.3 mg of [Pd(μ-Cl)($C_6H_4CH_2NMe_2$)]$_2$ (0.16 mmol) and 150 mg of **1b** (0.32 mmol) was added 4 mL of CH_2Cl_2. The solution was stirred for 30 min at room temperature. After removal of the solvent, the crude product was recrystallized from toluene/pentane to give 143 mg (60%) of the product. Anal. Calcd for $C_{42}H_{37}NOPClPd$: C, 67.75; H, 5.01; N, 1.88. Found: C, 68.33; H, 5.69; N, 1.78. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.64 (d, $^3J_{HH}$ = ca. 9.2, *H-4*), 7.64 (d, $^3J_{HH}$ = ca. 9.2, *H-10*), 7.24 (d, $^3J_{HH}$ = 8.6, *H-7*), 7.19 (*H-9*), 7.08 (*H-8*), 6.82 (d, $^3J_{HH}$ = 7.3, *H-L5*), 6.78 (*H-5*), 6.65 (t, $^3J_{HH}$ = 7.5, *H-L4*), 6.15 (t, $^3J_{HH}$ = 7.7, *H-L3*), 6.08 (t, $^3J_{HH}$ = 6.8, *H-L2*), 3.78 (d, $^4J_{PH}$ = 1.3, 2 H, *H-L7*), 3.40 (s, OC*H*$_3$), 2.68 (d, $^4J_{PH}$ = 2.5, *CH*$_3$-*L8*), 2.67 (d, $^4J_{PH}$ = 2.5, *CH*$_3$-*L9*). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 154.7 (*C-6*), 151.8 (*C-L1*), 148.8 (*C-L6*), 138.5 (*C-L2*), 134.6 (*C-2*), 130.6 (*C-4*), 129.1 (*C-3*), 127.6 (*C-10*), 127.2 (*C-7*), 124.5 (*C-L3*), 123.6 (*C-L4*), 122.2 (*C-L5*), 119.9 (*C-1*), 112.2 (*C-5*), 73.4 (*C-L7*), 55.3 (O*C*H$_3$), 50.8 (*C-L8*), 50.6 (*C-L9*). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 48.1 (s). MS (MALDI): 708.1 (M$^+$ − Cl, 100%).

Synthesis of PdCl(C$_6$H$_4$CH$_2$NMe$_2$)(1b′), 11. To a mixture of 59.7 mg of [Pd(μ-Cl)($C_6H_4CH_2NMe_2$)]$_2$ (0.108 mmol) and 150 mg of **1b′** (0.216 mmol) was added 4 mL of CH_2Cl_2. The solution was stirred for 30 min at room temperature. The solvent was distilled off to give a quantitative yield of the product. Anal. Calcd for $C_{58}H_{69}NOPClPd$: C, 71.89; H, 7.18; N, 1.45. Found: C, 71.93; H, 7.23; N, 1.39. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.63 (d, $^3J_{HH}$ = 8.3, *H-4*), 7.63 (d, $^3J_{HH}$ = 8.3, *H-10*), 6.89 (b, *H-5*), 6.69 (*H-L5*), 6.54 (t, $^3J_{HH}$ = 7.5, *H-L4*), 6.00 (t, $^3J_{HH}$ = 7.5, *H-L3*), 5.80 (b, *H-L2*), 3.65 (b, 1 H, *H-L7*), 3.51 (b, 1 H, *H-L7*), 3.33 (s, OC*H*$_3$), 2.65 (s, *CH*$_3$-*L8*), 2.53 (s, *CH*$_3$-*L9*), 1.08 (s, 18 H, C(C*H*$_3$)$_3$), 0.91 (s, 18 H, C(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 155.6 (*C-6*), 151.6 (*C-L1*), 148.3 (*C-L6*), 138.8 (*C-L2*), 134.5 (*C-2*), 130.4 (*C-4*), 128.9 (*C-3*), 127.7 (*C-10*), 124.4 (*C-L3*), 123.3 (*C-L4*), 121.8 (*C-L5*), 121.6 (*C-1*), 113.8 (*C-5*), 73.2 (*C-L7*), 56.3 (O*C*H$_3$), 50.6 (*C-L8*), 50.2 (*C-L9*), 35.1 (*C*(CH$_3$)$_3$), 34.7 (*C*(CH$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 49.6 (bs). MS (MALDI): 932.4 (M$^+$ − Cl, 100%).

For all of the chloride abstraction reactions that follow, below, NMR monitoring shows the reaction to be essentially quantitative. The weight losses arise from handling the relatively small amounts of noncrystalline material.

Synthesis of [Pd(C$_6$H$_4$CH$_2$NMe$_2$)(1b)](BArF), 12. A 60 mg amount of **10** (0.081 mmol) and 71.4 mg of NaBArF (0.081 mmol) were stirred for 30 min at room temperature in 3 mL of CH_2Cl_2. Filtration over Celite and washing with 0.5−1.0 mL of dichloromethane was followed by removal of the solvent to give 92 mg (72%) of the product. Anal. Calcd for $C_{74}H_{49}NOBF_{24}$-PPd: C, 56.53; H, 3.14; N, 0.89. Found: C, 57.40; H, 3.29; N, 0.94. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.88 (d, $^3J_{HH}$ = 9.0, *H-4*), 7.61 (d, $^3J_{HH}$ = 8.3, *H-10*), 7.44 (*H-4*), 7.27 (*H-9*), 6.98 (t, $^3J_{HH}$ = 7.7, *H-8*), 6.86 (d, $^3J_{HH}$ = 7.3, *H-L5*), 6.72 (*H-L4*), 6.48 (bd, $^3J_{HH}$ = 8.1, *H-7*), 6.16 (t, $^3J_{HH}$ = 7.9, *H-L3*), 5.94 (t, $^3J_{HH}$ = $^4J_{PH}$ = 7.1, *H-L2*), 4.56 (d, $^2J_{HH}$ = 14.1, *H-L7*), 3.48 (dd, $^2J_{HH}$ = 13.7, $^4J_{PH}$ = 3.6, *H-L7*), 3.39 (s, OC*H*$_3$), 2.91 (d, $^4J_{PH}$ = 3.2, *CH*$_3$-*L8*), 2.86 (d, $^4J_{PH}$ = 1.1, *CH*$_3$-*L9*). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 155.5 (*C-6*), 146.8 (*C-L6*), 140.9 (*C-L1*), 138.3 (*C-L2*), 132.8 (*C-4*), 132.7 (*C-2*), 132.2 (*C-3*), 128.4 (*C-10*), 127.5 (*C-8*), 127.0 (*C-7*), 126.7 (*C-9*), 126.5 (*C-L3*), 125.8 (*C-L4*), 125.2 (*C-1*), 124.0 (*C-L5*), 70.6 (*C-L7*), 65.8 (O*C*H$_3$), 51.6 (*C-L8*), 50.3 (*C-L9*). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 39.6 (s). MS (ESI): 707.50 (M$^+$ − BArF, 90%).

Synthesis of [Pd(C$_6$H$_4$CH$_2$NMe$_2$)(1b′)](BArF), 13. A 50 mg amount of **11** (0.052 mmol) and 45.7 mg of NaBArF (0.052 mmol) were stirred for 30 min at room temperature in 3 mL of CH_2Cl_2. Filtration over Celite and washing with 0.5−1.0 mL of dichloromethane was followed by removal of the solvent to give 61 mg (65%) of the product. Anal. Calcd for $C_{90}H_{81}NOBF_{24}$-PPd: C, 60.16; H, 4.54; N, 0.78. Found: C, 60.22; H, 4.74; N, 0.79. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.89 (d, $^3J_{HH}$ = 9.0, *H-4*), 7.62 (d, $^3J_{HH}$ = 8.3, *H-10*), 7.46 (*H-5*), 7.25 (*H-9*), 6.81 (d, $^3J_{HH}$ = 7.1, *H-L5*), 6.67 (t, $^3J_{HH}$ = 7.3, *H-L4*), 6.52 (d, $^3J_{HH}$ = 8.3, *H-7*), 6.04 (t, $^3J_{HH}$ = 7.7, *H-L3*), 5.76 (t, $^3J_{HH}$ = $^4J_{PH}$ = 7.1, *H-L2*), 4.54 (d, $^2J_{HH}$ = 13.3, 1 H, *H-L7*), 3.49 (dd, $^2J_{HH}$ = 13.5, $^4J_{PH}$ = 3.4, 1 H, *H-L7*), 3.39 (s, OC*H*$_3$), 2.94 (s, *CH*$_3$-*L8*), 2.85 (s, *CH*$_3$-*L9*), 1.08 (s, 18 H, C(C*H*$_3$)$_3$), 1.00 (s, 18 H, C(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2,125 MHz): δ 155.2 (*C-6*), 146.0 (*C-L6*), 141.6 (*C-L1*), 138.4 (*C-L2*), 133.2 (*C-2*), 133.0 (*C-4*), 131.9 (*C-3*), 128.5 (*C-10*), 126.4 (*C-9*), 126.4 (*C-7*), 126.3 (*C-L3*), 125.7 (*C-L4*), 125.4 (*C-1*), 123.6 (*C-L5*), 119.5 (*C-5*), 70.6 (*C-L7*), 65.8 (O*C*H$_3$), 51.6 (*C-L8*), 50.0 (*C-L9*), 35.1 (*C*(CH$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 43.8 (s). MS (ESI): 932.19 (M$^+$ − BArF, 100%).

Synthesis of [Pd(C$_6$H$_4$CH$_2$NMe$_2$)(1a)](BArF), 16. A 50 mg amount of **14** (0.070 mmol) and 62 mg of NaBArF (0.070 mmol) were stirred for 30 min at room temperature in 2 mL of CH_2Cl_2. Filtration over Celite and washing with 0.5−1.0 mL of dichloromethane was followed by removal of the solvent to give 58 mg (54%) of the product. Anal. Calcd for $C_{73}H_{47}NBF_{24}$-PPd: C, 56.85; H, 3.07; N, 0.91. Found: C, 57.76; H, 3.21; N, 0.99. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.20 (d, $^3J_{HH}$ = 8.6, *H-4*), 7.84 (d, $^3J_{HH}$ = 8.3, *H-10*), 7.81 (dd, $^3J_{HH}$ = 8.8 and 6.2, *H-5*), 7.34 (*H-9*), 7.25 (*H-6*), 6.80 (*H-L5*), 6.67 (*H-L4*), 6.66 (*H-8*), 6.21 (t, $^3J_{HH}$ = 7.7, *H-L3*), 6.15 (t, $^3J_{HH}$ = $^4J_{PH}$ = 7.7, *H-L2*), 6.11 (d, $^3J_{HH}$ = 8.3, *H-7*), 4.56 (d, $^2J_{HH}$ = 13.3, *H-L7*), 3.45 (dd, $^2J_{HH}$ = 13.3, $^4J_{PH}$ = 2.1, *H-L7*), 3.12 (bd, $^4J_{PH}$ = 2.8, *CH*$_3$-*L8*), 2.58 (s, *CH*$_3$-*L9*). ^{13}C NMR (CD_2Cl_2,125 MHz): δ 149.4 (*C-L1*), 149.2 (*C-1*), 145.1 (*C-L6*), 137.6 (*C-L2*), 134.5 (*C-3*), 132.0 (*C-2*), 131.3 (*C-4*), 129.5 (*C-9*), 128.3 (*C-10*), 128.0 (*C-8*), 127.5 (*C-7*), 127.5 (*C-5*), 127.4 (*C-L3*), 126.0 (*C-L4*), 124.4 (*C-L5*), 106.6 (*C-6*), 72.8

(30) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.
(31) Flack, H. D. *Acta Crystallogr.* **1983**, *A 39*, 876.
(32) Farrugia, L.J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(33) Murahashi, T.; Nagai, T.; Okuno, T.; Matsutani, T.; Kurosawa, H. *Chem. Commun.* **2000**, 1689−1690.

(*C-L7*), 51.5 (*C-L8*), 49.0 (*C-L9*). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 36.3 (s). MS (ESI): 677.80 (M^+ − BArF, 90%).

Synthesis of [Pd($C_6H_4CH_2NMe_2$)(1a′)](BArF), 17. A 60 mg amount of **15** (0.064 mmol) and 56.2 mg of NaBArF (0.064 mmol) were stirred for 30 min at room temperature in 3 mL of CH_2Cl_2. Filtration over Celite and washing with 0.5−1.0 mL of dichloromethane was followed by removal of the solvent to give 61 mg (65%) of the product. Anal. Calcd for $C_{89}H_{79}NBF_{24}$PPd: C, 60.50; H, 4.51; N, 0.79. Found: C, 60.73; H, 4.56; N, 0.91. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.18 (d, $^3J_{HH}$ = 8.6, *H-4*), 7.82 (*H-5*), 7.81 (*H-10*), 7.34 (t, $^3J_{HH}$ = 7.3, *H-9*), 7.24 (*H-6*), 6.80 (d, $^3J_{HH}$ = 7.3, *H-L5*), 6.72 (t, $^3J_{HH}$ = 7.5, *H-8*), 6.64 (t, $^3J_{HH}$ = 7.3, *H-L4*), 6.25 (d, $^3J_{HH}$ = 8.3, *H-7*), 6.11 (t, $^3J_{HH}$ = 7.7, *H-L3*), 6.05 (t, $^3J_{HH}$ = $^4J_{PH}$ = 7.7, *H-L2*), 4.59 (d, $^2J_{HH}$ = 13.3, *H-L7*), 3.46 (d, $^2J_{HH}$ = 13.3, *H-L7*), 3.19 (s, *CH*$_3$*-L8*), 2.62 (s, *CH*$_3$*-L9*), 1.05 (s, 18 H, C(C*H*$_3$)$_3$), 1.04 (s, 18 H, C(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 150.4 (*C-L1*), 150.3 (*C-1*), 144.5 (*C-L6*), 137.5 (*C-L2*), 134.6 (*C-3*), 132.1 (*C-2*), 131.1 (*C-4*), 129.6 (*C-9*), 128.5 (*C-10*), 127.8 (*C-7*), 127.7 (*C-5*), 127.2 (*C-L3*), 125.8 (*C-L4*), 124.1 (*C-L5*), 105.4 (*C-6*), 72.8 (*C-L7*), 51.5 (*C-L8*), 48.9 (*C-L9*), 35.1 (*C*(CH$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 39.5 (s). MS (ESI): 902.19 (M^+ − BArF, 100%).

Synthesis of PdCl($C_6H_4CH_2NMe_2$)(1d), 18. To a mixture of 35.7 mg of [Pd(μ-Cl)($C_6H_4CH_2NMe_2$)]$_2$ (0.065 mmol) and 60 mg of **1d** (0.129 mmol) was added 2 mL of CH_2Cl_2. The solution was stirred for 30 min at room temperature. After removal of the solvent the crude product was recrystallized from toluene/pentane. Yield: 76.1 mg (80%). Anal. Calcd for $C_{42}H_{34}N_2$PClPd: C, 68.21; H, 4.63; N, 3.79. Found: C, 68.14; H, 4.83; N, 3.58. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.13 (d, $^3J_{HH}$ = 8.6, *H-7*), 7.82 (d, $^3J_{HH}$ = 8.3, *H-10*), 7.63 (*H-4*), 7.61 (*H-9*), 7.51 (*H-8*), 7.04 (d, $^3J_{HH}$ = 8.6, *H-5*), 6.82 (d, $^3J_{HH}$ = 7.1, *H-L5*), 6.61 (*H-L4*), 6.05 (t, $^3J_{HH}$ = 7.7, *H-L3*), 5.76 (d, $^3J_{HH}$ = $^4J_{PH}$ = 7.1, *H-L2*), 4.04 (d, $^2J_{HH}$ = 13.5, *H-L7*), 3.61 (dd, $^2J_{HH}$ = 13.5, $^4J_{PH}$ = 3.2, *H-L7*), 2.83 (d, $^4J_{PH}$ = 2.6, *CH*$_3$*-L8*), 2.67 (d, $^4J_{PH}$ = 1.7, *CH*$_3$*-L9*). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 151.9 (*C-L1*), 149.9 (*C-L6*), 142.9 (*C-1*), 138.7 (*C-L2*), 134.9 (*C-3*), 133.0 (*C-2*), 130.5 (*C-7*), 129.3 (*C-9*), 129.3 (*C-4*), 128.1 (*C-10*), 127.1 (*C-5*), 124.8 (*C-L3*), 123.9 (*C-L4*), 122.3 (*C-L5*), 118.9 (*C*≡N), 112.4 (*C-6*), 73.6 (*C-L7*), 51.7 (*C-L8*), 49.8 (*C-L9*). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 49.7 (s). IR (Golden Gate): 3053 cm^{-1} (C−H arom.), 2224 cm^{-1} (C≡N). MS (HRMALDI): 703.1494 (M^+ − Cl, 25%, calc 703.1503).

Synthesis of [Pd($C_6H_4CH_2NMe_2$)(1d)](BArF), 19. A 54.6 mg amount of **18** (0.074 mmol) and 65.4 mg of NaBArF (0.074 mmol) were stirred for 30 min at room temperature in 3 mL of CH_2Cl_2. Filtration over Celite and washing with 0.5−1.0 mL of dichloromethane was followed by removal of the solvent to give 52 mg (45%) of the product. Anal. Calcd for $C_{74}H_{46}N_2$-BF_{24}PPd: C, 56.71; H, 2.96; N, 1.79. Found: C, 56.74; H, 3.15; N, 1.79. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.77 (d, $^3J_{HH}$ = 8.6, *H-4*), 7.58 (*H-9*), 7.57 (*H-5*), 7.34 (*H-8*), 7.00 (d, $^3J_{HH}$ = 8.6, *H-7*), 6.93 (d, $^3J_{HH}$ = 7.1, *H-L5*), 6.79 (t, $^3J_{HH}$ = 7.7, *H-L4*), 6.21 (t, $^3J_{HH}$ = 7.9, *H-L3*), 5.95 (t, $^3J_{HH}$ = $^4J_{PH}$ = 7.5, *H-L2*), 4.27 (bd, $^2J_{HH}$ = 12.6, *H-L7*), 3.84 (dd, $^2J_{HH}$ = 14.1, $^4J_{PH}$= 2.4, *H-L7*), 2.76 (bs, *CH*$_3$*-L8*), 2.70 (bs, *CH*$_3$*-L9*). ^{13}C NMR (CD_2Cl_2,125 MHz): δ 148.2 (*C-L6*), 146.2 (*C-1*), 145.0 (*C-L1*), 138.0 (*C-L2*), 136.0 (*C-3*), 132.0 (*C-2*), 131.6 (*C-4*), 130.9 (*C-9*), 129.1 (*C-10*), 128.3 (*C-7*), 126.3 (*C-L3*), 126.2 (*C-L4*), 125.2 (*C-5*), 123.9 (*C-L5*), 107.3 (*C-6*), 71.4 (*C-L7*), 51.7 (*C-L9*), 50.5 (*C-L8*). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 44.5 (s). IR (Golden Gate): 3063 cm^{-1} (C−H arom.), 2231 cm^{-1} (C≡N). IR (Nujol): 2240 cm^{-1} (C≡N). MS (ESI): 703.0 (M^+ − BArF, 80%), 735.1 (M^+ + MeOH − BArF, 100%).

Hydrosilylation of Styrene. To a mixture of 0.8 mg of [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ (2.1 μmol) and 8.2 μmol of MOP ligand was added 0.5 mL of styrene (4.33 mmol) and, after cooling to 5 °C, 0.53 mL of $HSiCl_3$ (5.3 mmol). The reaction solution was stirred at 5 °C and the product formation monitored by ^{1}H NMR.

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Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for **9**, including tables of positional and isotropic equivalent displacement parameters, anisotropic displacement parameters, calculated positions of the hydrogen atoms, bond distances, bond angles, and torsional angles. ORTEP figure showing the full numbering schemes. X-ray data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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