Contributions to the Enantioselective Heck Reaction Using MeO−Biphep Ligands. The Case Against Dibenzylidene Acetone

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It is shown that the Pd-catalyzed enantioselective Heck reaction of *p*-XC_6H_4OTf, X = OMe, H, CO_2Me, with dihydrofuran gives higher enantioselectivities when the chelating diphosphine MeO−Biphep, **1a**, is replaced with its disubstituted analogue 3,5-di-*tert*-butyl MeO−Biphep, **1b**. The phenylation of 5-methyl-2,3-dihydrofuran produces a new dihydrofuran containing a quaternary stereogenic center (ee, >98% with **1b**, ca. 20% with **1a**). Catalytic results for the reaction of phenyl triflate with dhf, together with stoichiometric oxidative addition reactions of aryl halides on Pd complexes of **1**, show that the use of Pd(dba)(**1**), dba = dibenzylidene acetone, slows the oxidative addition relative to the reaction in which the Pd(0) precursor is generated from $PdCl_2$(**1**) + $NaBH_4$. The solid-state structures for two PdI(aryl)(**1a**), **3**, derivatives, aryl = *p*-MeOOC−C_6H_4 (**3a**) and C_6F_5 (**3b**) are reported.

Introduction

The palladium-catalyzed Heck reaction,[1] which often consists of the introduction of an aryl substituent into a suitable olefin substrate, remains a subject of active interest.[2−5] There are now various protocols,[3b,6−8] most of which involve catalytic amounts of phosphine complexes. The reaction can be relatively slow and/or require elevated temperatures.[9−11] Increasingly, attention has turned to the enantioselective variant,[12] with Shibasaki,[12] Overman,[13] Hayashi,[14] and Pfaltz,[15] among others, reporting impressive results.

The mechanistic aspects of the Heck reaction are fairly well-known,[1−3] and although the groups of Amatore[16−18] and Brown[19] have made recent major contributions, new suggestions continue to appear.[20−22] Routinely (see Scheme 1), an aryl halogen (or triflate) starting material is oxidatively added to a Pd(0) complex (step a). This latter can be either added as a preformed complex, e.g., "Pd(L−L)(dba)", dba = dibenzylidene acetone, or generated in situ. The Pd(II) aryl complex that arises is frequently isolable.[1c] Olefin complexation at palladium (step b) is followed by insertion of the alkene into the Pd−C bond (step c). β-H elimination

(1) (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (b) Heck, R. F. *Comprehensive Organic Synthesis*; Pergamon: Oxford, 1991; Vol. 4. (c) Garrou, P.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

(2) de Meijere, A.; Meyer, F. E. *Angew. Chem.* **1994**, *106*, 2473−2506.

(3) (a) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2−7. (b) Cabri, W.; Candiani, I.; De Bernardinis, S.; Francalanci, F.; Penco, S. *J. Org. Chem.* **1991**, *56*, 5796−5800.

(4) Lemaire-Audoire, S.; Savignac, M.; Dupuis, C.; Genet, J. P. *Tetrahedron Lett.* **1996**, *37*, 2003−2006.

(5) Gibson, S. E.; Middleton, R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1743.

(6) Jeffery, T.; Galland, J. C. *Tetrahedron Lett.* **1994**, *35*, 4103−4106.

(7) Hillers, S.; Sartoti, S.; Reiser, O. *J. Am. Chem. Soc.* **1996**, *118*, 2087−2088.

(8) Rigby, J. H.; Huighes, R. C.; Heeg, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 7834−7835.

(9) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687−11688.

(10) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem.* **1998**, *110*, 492.

(11) Herrmann, W.; Brossmer, C.; Oefele, K.; Reisinger, C.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem.* **1995**, *107*, 1989−1992.

(12) Sato, Y.; Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1989**, *54*, 4738. Ohrai, K.; Kondo, K.; Sodeoka, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1994**, *116*, 11737−11748. Oshima, T.; Kagechika, K.; Adachi, M.; Sodeoka, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7108−7116.

(13) Abelman, M. M.; Kado, N.; Overman, L. E.; Sarkar, A. K. *SYNLETT* **1997**, 1469. Overman, L. E.; Link, J. T. In *Metal Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, 1998; p 239, and references therein.

(14) (a) Ozawa, F.; Kubo. A.; Matsumoto, Y.; Hayashi, T.; Nishioka, I.; Yanagi, K.; Moriguchi, K. *Organometallics* **1993**, *12*, 4188. (b) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 1417−1419.

(15) Pfaltz, A. *Acta Chim. Scand.* **1996**, *50*, 189−194. Loiseleur, O.; Meier, P.; Pfaltz, A. *Angew. Chem.* **1996**, *108*, 218.

(16) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375−8384.

(17) (a)Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Orgamometallics* **1993**, *12*, 3168−3178. (b) Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc.* **1993**, *115*, 9531−9541.

(18) Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176−5185.

(19) Hii, K. K.; Claridge, T. D. W.; Brown, J. M. *Angew. Chem.* **1997**, *109*, 1033−1036. Brown, J. M.; Hii, K. K. *Angew. Chem.* **1996**, *108*, 679. Brown, J. M.; Perez-Torrente, J.; Alcock, N.; Clase, H. J. *Organometallics* **1995**, *14*, 207. Deeth, R. J.; Smith, A.; Hii, K. K.; Brown, J. M. *Tetrahedron Lett.* **1998**, *39*, 3229−3232.

(20) Shaw, B. L. *New J. Chem.* **1998**, 77.

(21) Shaw, B. L.; Perera, S. D.; Staley, E. A. *J. Chem. Soc., Chem. Commun.* **1998**, 1361.

(22) Beller, M.; Fischer, H.; Kühlein, K.; Reisinger, C. P.; Herrmann, W. *J. Organomet. Chem.* **1996**, *520*, 257−259.

(23) (a) Trabesinger, G.; Albinati, A.; Feiken, N.; Kunz, R. W.; Pregosin, P. S.; Tschoerner, M. *J. Am. Chem. Soc.* **1997**, *119*, 6315. (b) Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502−5503. (c) Rajanbabu, T. V.; Ayers, T. A.; Caasalnuovo, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 4101. (d) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310−312. (e) Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.

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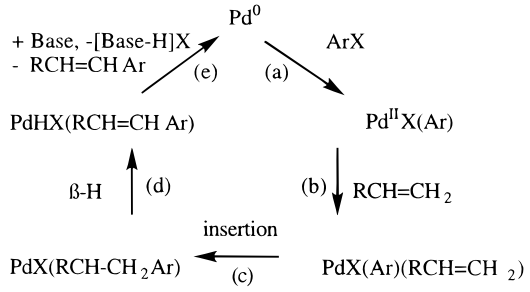
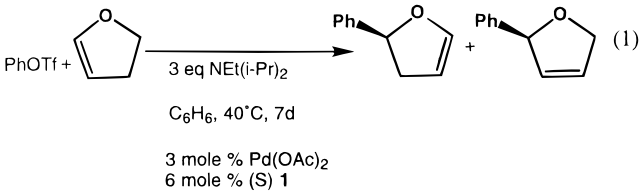
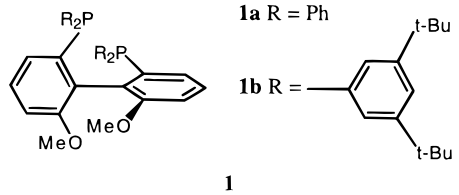
Scheme 1



(step d) and olefin decomplexation (step e) afford the organic product. The palladium hydride generated reacts with added base (NEt_3 or a Hünig base are commonly used) to regenerate the Pd(0) complex.

We have recently reported[23a] results for the enantioselective Heck addition of phenyl triflate to dihydrofuran (dhf) using the axially chiral MeO−Biphep ligand, **1b**, eq 1.[23] The relatively small olefin dhf has become





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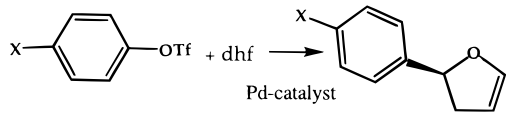
something of a test material for this reaction.[14,15] On the basis of the observed enantiomeric excesses, ligand **1b** is better than **1a**. In view of the continuing developments in Heck chemistry[10,11,20−22] we have expanded our studies to include new structural and catalytic aspects involving **1** and report here on (i) an extension of the *m*-di-*tert*-butyl effect on enantioselectivity, (ii) the rate reduction due to the use of dba, and (iii) the unexpected instability of several aryl intermediates.

Results and Discussion

The *m*-Di-*tert*-butyl Effect. Our new results for the palladium-catalyzed Heck reaction of *p*-XC_6H_4OTf, X = OMe, H, CO_2Me, with dhf, using **1** as auxiliary, are summarized in Table 1. The catalyst, $Pd(OAc)_2$ /NEt(i-Pr)$_2$ /**1**, in benzene at 40 °C, requires several days, with yields between 42% and 76%. The ee's using **1b** (91−99%) are always better than those found for **1a** (71−87%). This is consistent with the *m*-di-t-Bu effect on enantioselectivity described earlier[23a] and with other reports for B,[23b] Rh,[23c] Al,[23d] and Pd[23e] based catalysts containing 3,5-substituted aryl groups. Interestingly, for both **1a** and **1b** the *p*-OMe triflates give much lower ee's. Moreover, for **1b**, the reaction of the *p*-OMe derivative is ca. 5 times faster than for the CO_2Me analogue. Jutand and Mosleh[24] find the oxidative addition with

(24) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810−1817.

Table 1. Enantiomeric Excesses in the Heck Chemistry[a]

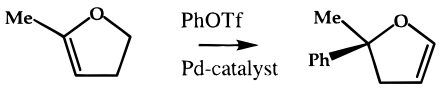


ligand	X	yield	ee
1a	H	52%	87
	COOMe	61%	87
	OMe	42%	71
1b	H	70%	99
	COOMe	76%	99
	OMe	57%	91

[a] $Pd(OAc)_2$, **1**, C_6H_6, dhf, PhOTf, and NEt(i-Pr)$_2$, 40 °C.

$Pd(PPh_3)_4$ to be faster when the aryl triflate has electron-*withdrawing* groups.

We have also studied the reaction of phenyl triflate with the trisubstituted olefin, 5-methyl 2,3-dihydrofuran, eq 2:



1a ee = ca 20% **1b** ee = > 98% (2)

The reaction is very slow (even at 70 °C) and the isolated yield only 38%; however, the ee with **1b** is excellent. This 5-methyl 2,3-dihydrofuran reaction is the most marked example of the meta dialkyl effect yet observed and represents a relatively rare example of an enantioselective intermolecular Heck reaction which generates a new fully substituted stereogenic center. These few additional catalytic experiments are further support for the existence of the *m*-di-*tert*-butyl effect.

Is dba Advantageous in Enantioselective Heck Chemistry? During our catalytic studies comparing **1a** with **1b** we tested several palladium precursors and noticed that the reactions starting from Pd(0)−dba complexes seemed sluggish. To confirm this, we compared the rates of product formation in the catalytic runs starting from Pd(dba)(**1a,b**),[23] **2**, with those from Pd(0) complexes generated by reducing chloro-derivatives in situ with $NaBH_4$.

$$Pd(dba)(\mathbf{1a}) + PhOTf + dhf \xrightarrow[\text{acetone, 40 °C}]{} \text{no reaction after 72 h} \quad (3)$$

$$PdCl_2(\mathbf{1a}) + PhOTf + dhf \xrightarrow[\text{acetone, 40 °C}]{NaBH_4} 70\%\ \text{conversion after 72 h} \quad (4)$$

$$Pd(dba)(\mathbf{1b}) + PhOTf + dhf \xrightarrow[\text{acetone, 40 °C}]{} \text{no reaction after 72 h} \quad (5)$$

$$PdCl_2(\mathbf{1b}) + PhOTf + dhf \xrightarrow[\text{acetone, 40 °C}]{NaBH_4} 44\%\ \text{conversion after 67 h} \quad (6)$$

Equations 3−6 show this chemistry, and Figure 1 represents the development of organic product as a function of time using several catalyst precursors. The catalytic reactions were carried out at 313 K, but the experiments for the relative kinetics, at room temperature, to facilitate monitoring by NMR methods. From

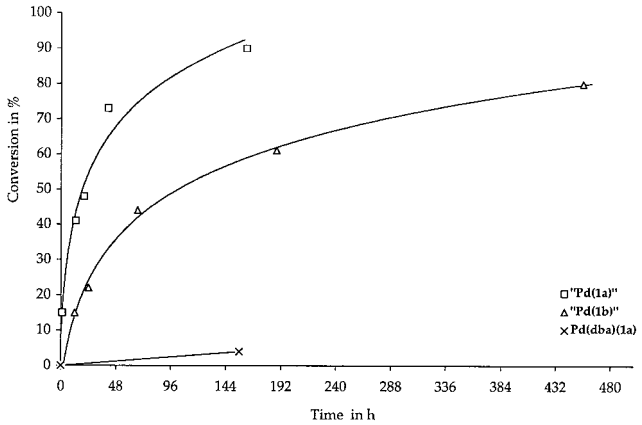


Figure 1. Development of the 2-phenyldihydrofuran organic product as a function of time, for the Pd-catalyzed Heck reaction of dhf with PhOTf. The upper curves arise from the reactions of "Pd(**1a**)" (fastest) and "Pd(**1b**)", whereas the bottom curve shows that little product is formed from Pd(dba)(**1a**) after ca. 100 h.

Figure 1 it can be seen that the complexes $PdCl_2$(**1a** or **1b**) plus borohydride slowly catalyze the reaction, but the dba complex is hardly active. Since some organic substrates will not tolerate reaction at elevated temperature, the correct choice of catalyst precursor can be critical. With the dba precursor at ambient temperature, there is, practically speaking, no reaction.

Interestingly, the reaction with **1b** is slower than with **1a** presumably for steric reasons. The Pd(0) complex of **1a** is new (see Experimental Section for this complex plus benzoquinone and pentenedione analogues), whereas we have reported the analogue for **1b** previously.[25]

To shed further light on the question of reaction rates using dba, we have followed the stoichiometric room-temperature oxidative addition of PhI, in acetone, as shown in eqs 7 and 8:

$$PdCl_2(\mathbf{1a}\text{ or }\mathbf{1b}) + Ph{-}I \xrightarrow[\text{acetone/rt}]{NaBH_4} PdI(Ph)(\mathbf{1a}\text{ or }\mathbf{1b}) \quad (7)$$
ca. 100% in < 3 min

$$Pd(dba)(\mathbf{1a}\text{ or }\mathbf{1b}) + Ph{-}I \rightarrow$$
no reaction after 144 h (8)

The reaction of the *p*-cyanobromo compound, eqs 9 and 10, was also investigated.

$$PdCl_2(\mathbf{1a}) + p\text{-}NCC_6H_4Br \xrightarrow[\text{acetone}]{NaBH_4} PdBr(p\text{-}NCC_6H_4)(\mathbf{1a}) \quad (9)$$

$$Pd(dba)(\mathbf{1a}\text{ or }\mathbf{1b}) + p\text{-}NCC_6H_4Br \rightarrow$$
no reaction after 120 h (10)

The chemistry of eq 9 is complete in < 1 h, whereas the reaction does not proceed using the dba compound. Although the isolated yield of $PdBr(p\text{-}NCC_6H_4)$(**1a**) is 70%, monitoring its progress via NMR suggests that the yield is essentially quantitative. Given these drastic differences in rate for both PhI and $p\text{-}NCC_6H_4Br$, we again conclude that for **1a,b** there is no advantage in using dba to stabilize the zero oxidation state.

Apart from the reduced reactivity of the dba complex, the relatively rapid oxidative addition of PhI using the BH_4^- route suggests that this step would most likely *not* be rate determining if one were to use the iodide, and not the triflate, as substrate.

Detailed kinetic studies by Amatore et al. show that, in the oxidative addition reaction using PhI, "Pd(Binap)" is more reactive than Pd(dba)(Binap).[18] Further, these authors note that for a variety of chelating diphosphines, Pd(dba)(L−L), the dba complex is "involved in an endergonic equilibrium with the less ligated complex Pd(L−L) and dba". When $NaBH_4$ is used to generate "Pd(**1**)", a more active species[26] is directly produced, and consequently one finds a faster reaction.

We have also checked the rates of the stoichiometric oxidative addition reaction of PhI using $Pd(dba)(PPh_3)_2$ and $Pd(PPh_3)_4$ and, in agreement with Amatore,[17a] find that both of these react relatively quickly (<3 min[27]) to form the *trans*-$PdI(Ph)(PPh_3)_2$ product.

Since the borohydride reduction affords Cl^- ions, it is possible that our observed rate acceleration arises via an electron-rich Pd(0) anion, e.g., $PdCl_x(\mathbf{1})^{x-}$, $x = 1, 2$, as suggested previously for PPh_3 derivatives.[17b] In any case, the slower reactions of the dba complexes are probably due to the reduced nucleophilicity of the Pd-(0), since dba, an α,β-unsaturated ketone, can withdraw electron density via π-back-bonding.

The above results show that dba is likely to be most detrimental in enantioselective Heck chemistry, where *bidentate* ligands are routinely employed. We do not suggest that, generally, the $PdCl_2(L{-}L)/NaBH_4$ route must lead to faster catalysis in all cases, since the structure of the substrate olefin cannot be neglected. However, for reactions in which the olefin substrate employed is a poorer ligand than dba, its presence could well lead to rate reductions. Our proposed borohydride route represents a simple alternative.

Structural Studies. As suggested by Scheme 1, the oxidative addition of PhI is expected to produce PdI-(aryl)(**1a**) as an intermediate. Since this oxidative addition reaction may not be rate determining (vida supra), we tried to prepare and isolate both $PdI(C_6H_5)$-(**1a**) and $PdI(p\text{-}OMe\text{-}C_6H_4)$(**1a**) using the $NaBH_4$ reduction route, followed by addition of, for example, PhI. However, our efforts were thwarted by decomposition to the diiodo derivative, PdI_2(**1a**), which could be isolated and characterized. There is no sign of palladium black. The same diiodide was formed when **1a** was added to $PdI(C_6H_5)(TMEDA)$.[28] This alternative synthetic approach, i.e., displacement of TMEDA from a complex that already contains the required aryl, suggests that the problem does not arise from decomposition due to Pd(0). Consequently, in the absence of olefin substrate, these two aryl products are inherently unstable. However, we have been successful in isolating several compounds of the type $PdI(p\text{-}X{-}C_6H_4,)$(**1a**), X

(25) Tschoerner, M.; Trabesinger,G.; Albinati, A.; Pregosin, P. S. *Organometallics* **1997**, *16*, 3447.

(26) A similar approach to generating Pd(0) in solution is given by Amatore and co-workers in ref 17b.

(27) In ref 17a, $Pd(PPh_3)_4$ is reported to react ca. 10 times faster than $Pd(dba)(PPh_3)_2$; however both react on the seconds time scale, so that our NMR measurements were not quick enough to make this distinction.

(28) de Graaf, W.; van Wegen, J.; Boersma, J.; Spek, A.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 275−277.

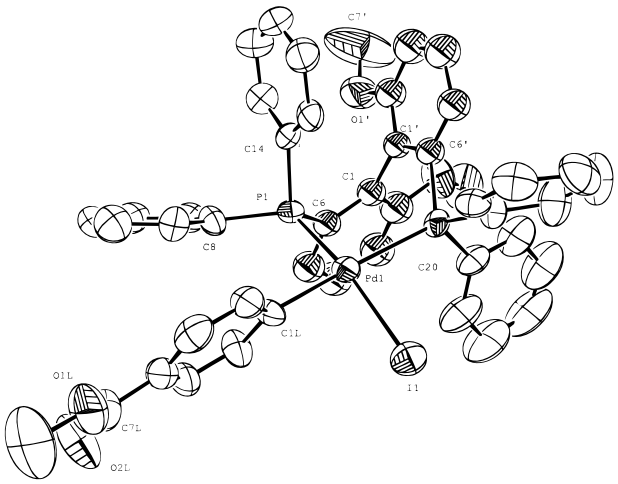


Figure 2. ORTEP plot of **3a**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 3a and 3b

	3a	3b
Pd−P1	2.262(3)	2.2798(7)
Pd−P2	2.397(3)	2.3502(7)
Pd−C1L	2.04(1)	2.062(3)
Pd−I	2.646(1)	2.6284(3)
P1−Pd−I	168.98(8)	174.63(2)
P2−Pd−C1L	175.4(3)	175.73(8)
P1−Pd−P2	91.8(1)	93.10(3)
P1−Pd−C1L	92.4(3)	91.15(8)
P2−Pd−I	92.12(8)	89.21(2)
I−Pd−C1L	84.2(3)	86.52(7)

= CO_2Me, CN, NO_2, as well as PdI(C_6F_5)(**1a**), all of which contain electron-withdrawing groups on the aryl moiety. These aryl complexes could be most effectively prepared by adding **1a** to the known complexes PdI(*p*-XC_6H_4)(TMEDA)[28] (although the oxidative addition also works, see eq 9), and we have determined the structures for two of these, PdI(*p*-(CO_2Me)C_6H_4)(**1a**), **3a**, and PdI(C_6F_5)(**1a**), **3b**. It was hoped that these X-ray results might provide a hint with respect to the lack of stability for both PdI(C_6H_5)(**1a**) and PdI(*p*-OMe-C_6H_4)(**1a**).

Suitable crystals of **3a** were obtained from CH_2Cl_2/Et_2O, and a view of the molecule is given in Figure 2. The local coordination geometry is pseudo-square-planar with the two P atoms, the iodide, and C1L comprising the immediate coordination sphere. The Pd−P bond lengths, Pd−P1 2.262(3) Å and Pd−P2 2.397(3) Å, are quite different, with the latter at the upper end of the literature range, supporting a large trans influence for the *p*-$MeO_2C-C_6H_4$ ligand (see Table 2). This long Pd−P bond is interesting in connection with the observed relative instability of PdI(C_6H_5)(**1a**) in solution. Perhaps without the electron-withdrawing ester group, the Pd−P bond trans to the aryl (e.g., in either PdI(C_6H_5)(**1a**) or PdI(*p*-OMe-C_6H_4)(**1a**)) might be even longer and perhaps more reactive. Hartwig and co-workers[30] report similar Pd−P distances, 2.283(2) and 2.391(2) Å, for the structure of the ferrocene diphosphine derivative Pd(NPh_2)(*p*-$Me_2N-C_6H_4$)(dppf), which contains the *p*-(dimethylamino) donor. Herrmann et al.[31] find 2.2385(5) and 2.3504(5) Å Pd−P distances in the somewhat less crowded bis(diphenylphosphino)propane derivative Pd-Cl(Ph)(dppp), suggesting that the phenyl ligand does not always exercise such a marked trans influence. The Pd−C1L, 2.04(1) Å, and Pd−I1, 2.646(1) Å, separations in **3a** are normal.

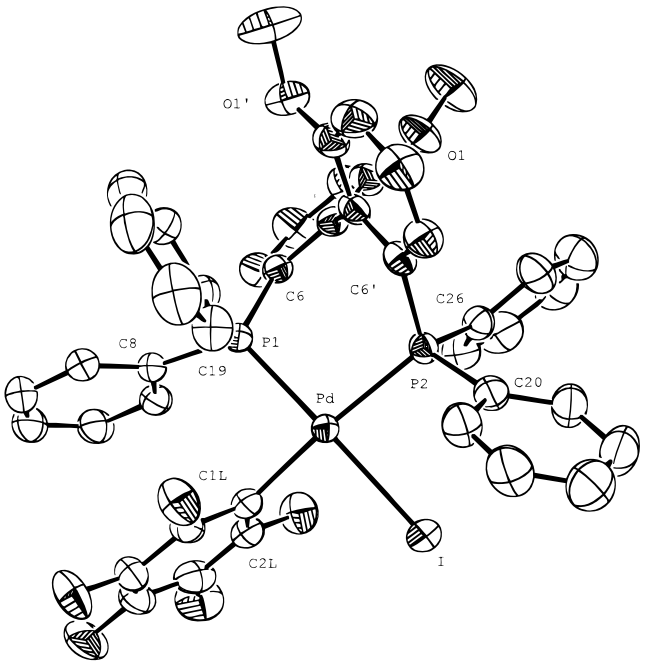


Figure 3. ORTEP plot of **3b**.

To confirm the possible correlation between Pd−P bond length and trans influence of the aryl, an aryl complex with a different trans influence was needed. Given the larger number of electron-withdrawing groups on the C_6F_5 ring, it seemed likely that this ligand would possess a smaller trans influence than that of the *p*-$MeO_2C-C_6H_4$ analogue. Crystals of **3b** were obtained from CH_2Cl_2/Et_2O, and a view of this molecule is given in Figure 3. The local coordination geometry is again pseudo-square-planar, with the two P atoms, the iodide, and C1L completing the immediate coordination sphere.

The Pd−P bond lengths in **3b**, Pd−P1 2.2798(7) Å and Pd−P2 2.3502(7) Å, are different, with the latter distance now much shorter than the corresponding separation in **3a**. This observation is in agreement with the idea that increasing the number of electron-withdrawing groups on the phenyl weakens the σ-donor component and thus the trans influence.

Figure 4 shows the structure of **3a** superimposed on that for **3b**.[32] It appears that one of the P-phenyls of **3b**

(29) Tschoerner, M.; Kunz, R. W.; Pregosin, P. S. To appear in *Magn. Reson. Chem.*

(30) Driver, M. S.; Hartwig, J. F. *Organometallics* **1997**, *16*, 5706−5715.

(31) Herrmann, W. A.; Brossmer, C.; Priermeier, T.; Oefele, K. *J. Organomet. Chem.* **1994**, *481*, 97−108.

(32) There are several interesting details for both structures: for **3a** the phenyl ring makes an angle of ca. 73° with the P−Pd−P plane, and there is a modest tetrahedral distortion in that the P1(−0.16 Å) and I1(−0.14 Å) are slightly below this plane and P2(0.10 Å) and C1L-(0.13 Å), slightly above. The I1−Pd−P1 and I1−Pd−C1L angles are relatively small, ca. 169° and 84°, respectively, suggesting some relief of steric strain by moving the iodide toward the phenyl moiety. The P−Pd−P bite angle is ca. 92°. For **3b** the C_6F_5 ring makes an angle of ca. 70° with the five atoms of the coordination plane, and, as in **3a**, there is a tetrahedral distortion, albeit a smaller one: P1(ca. −0.06 Å) and I1(ca. −0.06 Å) are slightly below, and P2(ca. 0.03 Å) and C1L-(ca. 0.04 Å), slightly above the coordination plane. The Pd−C1L, 2.062-(3) Å, and Pd−I1, 2.6284(3) Å, separations are as expected. In contrast to **3a** the coordination angles in **3b** do not deviate markedly from those expected for a slightly distorted square planar geometry. The P−Pd−P angle is ca. 93°.

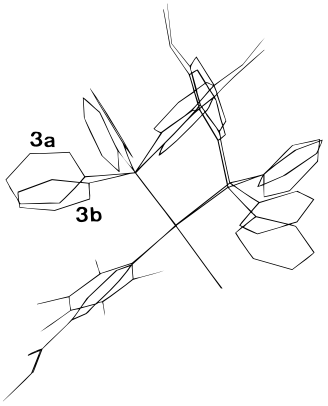
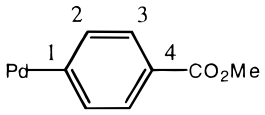


Figure 4. Superimposed structures of **3a** and **3b**.

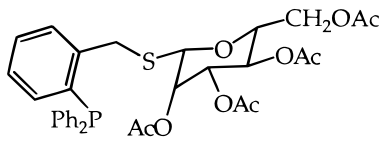
almost stacks with the C_6F_5 ring. The distances between the two rings (e.g., C8−C1L, 3.09 Å, C9−C2L, 3.07 Å, C13−C6L, 3.6 Å) would be roughly correct for such an interaction. Generally speaking, arene−arene stacking is found increasingly[33] and is thought to be favored when one ring is relatively electron poor.[34] Specifically, phenyl−perfluorophenyl stacking is now well-known.[35]

^{13}C NMR Spectroscopy. Since we observe the diiodo product, i.e., the aryl is lost, we were interested in establishing whether the ipso-aryl ^{13}C resonance, C1, might somehow reflect this effect. As shown in Figure



5, this resonance is best assigned via a long-range ^{13}C,^{1}H correlation to the proton of C3. This meta proton is correlated to both the ipso carbon and the ester carbonyl carbon (CO_2Me), δ = ca. 168, via three-bond interactions and thus readily reveals the appropriate cross-peaks. The use of long-range carbon−proton correlations is more or less unknown in organometallic chemistry, and we suggest that this methodology has potential, especially where carbons with long T_1 values are to be measured.

The observed chemical shift for C1 in **3a**, δ = 167.2, is at fairly high frequency. Relative to the model compounds PdI(*p*-$CO_2MeC_6H_4$)(TMEDA), δ = 156.6 (C1 trans to N), and PdI(*p*-$CO_2MeC_6H_4$)(**4**), δ = 159.4 (C1



4

trans to thioether-S), the observed δ = 167.2 ppm is consistent with the expected trans influences for these three different donor ligands, i.e., P > S > N. Further, this high-frequency position is not far from those found

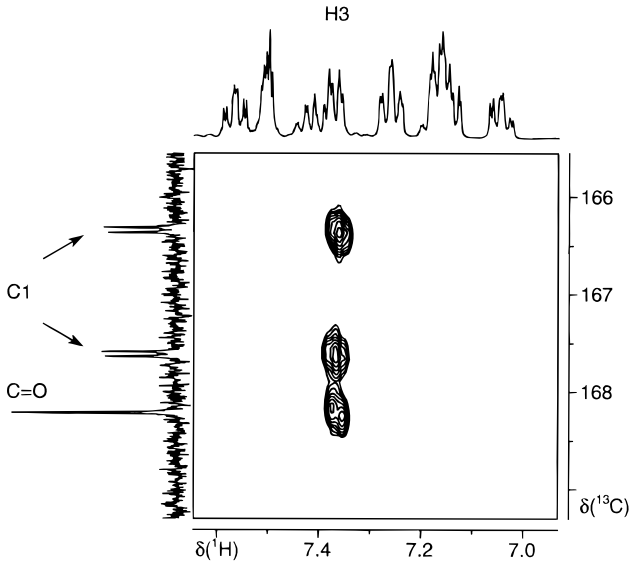


Figure 5. Long-range ^{13}C,^{1}H correlation for **3a** showing the assignment of (a) the aryl ipso-carbon (doublet of doublets) and (b) the ester carbonyl, via the appropriate cross-peaks. This correlation method makes use of the three-bond coupling constants, $^{3}J(^{13}C,^{1}H)$. Note that the two doublets for the ipso-carbon arise due to one relatively large $^{2}J(P,C)_{trans}$ value, 128 Hz, plus a modest $^{2}J(P,C)_{cis}$ value of 6 Hz.

for PhLi, δ = 174.6−186.8, in a variety of solvents.[36] Consequently, we interpret our observed chemical shift value of 167.2 ppm to suggest increasing anionic character in the Pd−C bond, with a concomitant larger trans influence. While this NMR result cannot be taken as a direct measure of stability, both this chemical shift and the X-ray results hint at reasons for the instability of PdI(C_6H_5)(**1a**) and PdI(*p*-OMe−C_6H_4)(**1a**); that is, both the σ-bound carbon and the trans P-donor are labilized.

Comment. Before concluding, we, return to the observed 71% ee found for *p*-OMe−C_6H_4OTf with **1a**, relative to the 87% ee for the C_6H_5 analogue. Although a reduction in ee when a methoxy group is introduced is known,[14b,37] it demonstrates that this substituent markedly affects the catalysis. Further, the *p*-OMe−C_6H_4OTf reacts ca. 5 times faster than the *p*-CO_2Me−C_6H_4OTf analogue. Admittedly, these catalytic results and our observations in the preparative chemistry cannot (yet) be tied together with certainty; nevertheless, it seems clear that there are important electronic effects at work not only in the Heck reaction but also in the Pd-coordination chemistry.

In summation, we find (i) additional support for the *m*-di-*tert*-butyl effect on enantioselectivity in the Heck reaction, (ii) that for **1a**,**b** dba significantly slows the Heck reaction (and specifically, the oxidative addition), and (iii) that, for some aryl derivatives, both the σ-bound carbon and the trans P-donor are labilized.

Experimental Section

General Comments. All reactions were done in an atmosphere of dry argon using standard Schlenk techniques.

(33) Barbaro, P. Pregosin, P. S.; Salzmann, R.; Albinati, A.; Kunz, R. W. *Organometallics* **1995**, *14*, 5160.

(34) Bahl, A.; Grahn, W.; Stadler, S.; Feiner, F.; Bourhill, G.; Bräuchle, C.; Reisner, A.; Jones, P. G. *Angew. Chem.* **1995**, *107*, 1587.

(35) Coates, G. W.; Dunn, A. R.; Hennling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641−3649, and references therein.

(36) Wehman, E.; Jastrebzyski, J. T. B. H.; Ernsting, J. M.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1988**, *353*, 133−143.

(37) Casalnuovo, A. L.; Rajanbabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869−9882. Schnyder, A.; Togni, A.; Wiesli, U. *Organometallics* **1997**, *16*, 255−260, and references therein.

Solvents were freshly distilled from established drying agents under argon prior to use. The complexes [PdX(TMEDA)(aryl)] were prepared by the method of de Graf et al.[28] NMR spectra were measured using Bruker DPX300 and DRX400 MHz spectrometers. Two-dimensional NMR spectra were measured as described previously.[23,33]

Catalytic Heck Reaction of $PdCl_2$(1a) with $NaBH_4$, dhf, and PhOTf in Acetone-d_6. $PdCl_2$(**1a**) (7.6 mg, 3 mol %) was dissolved in 0.6 mL of acetone-d_6 in a 5 mm NMR tube under Ar at −30 °C and reacted with $NaBH_4$ (0.76 mg), dhf (126 μL), PhOTf (53 μL), and *N*,*N*-diisopropylethylamine (170 μL). The reaction was followed by NMR at room temperature (conversion/time: 15%/1 h, 41%/13 h, 48%/20 h, 90%/162 h). The run with $PdCl_2$(**1b**) was performed in the same way (conversion/time: 15%/12 h, 22%/24 h, 44%/67 h, 61%/188 h, 80%/456 h).

Catalytic Heck Reaction of Pd(dba)(1a) with dhf and PhOTf in Acetone-d_6. Pd(dba)(**1a**) (9.2 mg, 3 mol %) was dissolved in 0.6 mL of acetone-d_6 at room temperature in a 5 mm NMR tube under Ar. Substrate dhf (126 μL), PhTfl (53 μL), and *N*,*N*-diisopropylethylamine (170 μL) were then added. The tube was then sealed, and the reaction was followed by NMR. A 4% conversion was reached after 156 h.

Using Pd(dba)(**1b**) as catalyst precurser no reaction was observed after 96 h.

Reaction of $PdCl_2$(1b) with $NaBH_4$ and PhI. $PdCl_2$(**1b**) (12.1 mg) was dissolved in 0.6 mL of acetone-d_6 at −30 °C and reacted with $NaBH_4$ (0.76 mg) (formation of H_2 and NaCl). PhI (2 μL) was then added to the dark red-brown suspension. The color changed to orange while warming the reaction to room temperature. ^{31}P NMR shows the formation of PdI(C_6H_5)(**1b**) within 3 min. This compound is not stable for prolonged periods in solution (PdI_2(**1b**) is the observed product).

Reaction of Pd(dba)(1a) with BrC_6H_4CN in THF. The reaction was carried out under Ar in a 5 mm NMR tube with a sealed D_2O-filled capillary for locking. Pd(dba)(**1a**) (4 mg, 3.7 μmol) was disolved in 0.6 mL of THF, and 1.2 mg (2 equiv) of BrC_6H_4CN was then added. The reaction was followed by ^{31}P NMR. No conversion to product was observed at room temperature during 120 h. No reaction was observed in runs at room temperature with Pd(dba)(**1a**)/PhI or Pd(dba)(**1b**)/PhI.

Arylation of 2,3-dhf Using *p*-MeO−C_6H_4OTf. A Schlenk-ampule was loaded with $Pd(OAc)_2$ (6.7 mg, 3 mol %) and (*R*)-**1b** (61.9 mg, 6 mol %), and these solids were dissolved in 4.5 mL of benzene. After addition of dhf (378 μL, 5 mmol), the solution was stirred at 40 °C for 40 min, and the solution was then treated with *p*-MeO−C_6H_4−OTf (178 μL, 1 mmol) and EtN(i-Pr)$_2$ (510 μL, 3 mmol). The solution was then degassed and stirred under Ar at 40 °C. The progress of the reaction was monitored by NMR. After 24 h 89% conversion was observed. After 36 h 100% conversion was observed. One observes 91% of (−)-2-(*p*-MeO−C_6H_4)-2,3-dhf, plus 9% (−)-2-(*p*-MeO−C_6H_4)-2,5-dhf. The reaction mixture was added to 200 mL of pentane and filtered off. The resulting solution was washed with 0.1 mol/L HCl, 10% K_2CO_3 solution, dried over $MgSO_4$, and then concentrated (rot. evap.). The crude product was purified by column chromatography (silica, hexane:ethyl acetate 95:5). Yield: 133 mg (75.5%) of (−)-2-(*p*-MeO−C_6H_4)-2,3-dhf: MS (EI$^+$, *m*/*e*): 176.1 [M$^+$]. HPLC: ChiraGrom 1 hexane: i-PrOH 99:1, 0.3 mL/min, (+)-isomer t_R = 6.2, (−)-isomer t_R = 6.9, gave 91.4% ee, opt. rotation $[\alpha]_D = -92.7°$, *c* = 0.51 $CHCl_3$.^{1}H NMR (300.13 MHz, $CDCl_3$): 2.64 (m, 1H), 3.06 (m, 1H), 3.83 (s, 3H, OMe), 4.98 (m, 1H), 5.49 (m, 1H, H2), 6.45 (m, 1H), 6.91 (m, 2H^{ar}), 7.32 (m, 2H^{ar}). ^{13}C{^{1}H} (75.47 MHz, $CDCl_3$): 159.5 (C^{para}), 145.5 (C^{olefin}), 135.4 (C^{ipso}), 127.4 (C^{orto}), 114.2 (C^{meta}), 99.4 (C^{olefin}), 82.5 (C2), 55.7 (OMe), 37.9 (C3). (+)-2-(*p*-MeO−C_6H_4)-2,5-dhf: ^{1}H NMR (300.13 MHz, $CDCl_3$): 3.82 (s, 3H, OMe), 4.7−4.8 (m, 1H, H5), 4.8−4.9 (m, 1H, H5′), 5.75 (m, 1H), 5.88(m, 1H), 6.07 (m, 1H), 6.90 (m, 2H^{ar}), 7.25 (m, 2H^{ar}). ^{13}C{^{1}H} (75.47 MHz, $CDCl_3$): 159.8 (C^{para}), 134.5 (C^{ipso}), 130.4 (C^{olefin}), 128.3 (C^{orto}), 127.1 (C^{olefin}), 114.3 (C^{meta}), 87.9 (C2), 75.9 (C5), 55.7 (OMe). The same procedure with (*S*)-**1a** gave (+)-2-(*p*-MeO−C_6H_4)-2,3-dhf, 74 mg (42%) with 71% ee.

Arylation of 2,3-dhf Using *p*-MeOOC−C_6H_4OTf. $Pd(OAc)_2$ (6.7 mg, 3 mol %) and (*R*)-(**1b**) (61.9 mg, 6 mol %) were dissolved in 4.5 mL of benzene, dhf (378 μL, 5 mmol) was added, and the solution was stirred for 40 min. After the addition of *p*-MeOOC−C_6H_4OTf (195 μL, 1 mmol) and EtN(i-Pr)$_2$ (510 μL, 3 mmol), the solution was degassed and stirred under Ar at 40 °C. The progress of the reaction was monitored by NMR: 24 h, 8% conv.; 40 h, 68.8% conv.; 76.5 h, 99% conv. (78% 2-Ar-2,3-dhf, 21% 2-Ar-2,5-dhf). The reaction mixture was added to 200 mL of pentane and filtered off. The solution was washed with 0.1 mol/L HCl and 10% K_2CO_3 solution, dried over $MgSO_4$, and concentrated (rot. evap.). The residue was chromatographed on SiO_2 with hexane/ethyl acetate, 95:5. Yield: 115.2 mg (56.5%) of (−)-2-(*p*-MeCOO−C_6H_4)-2,3-dhf and 44.5 mg (21.8%) of 2-(*p*-MeCOO−C_6H_4)-2,5-dhf. Total: 78.3%. Anal. Calcd (found) for $C_{12}H_{12}O_3$ (MW = 204.2 g/mol): C, 70.58 (70.51); H, 5.92 (5.82). MS (EI$^+$, *m*/*e*): 204.1 [M$^+$]. 2-(*p*-MeOOC−C_6H_4)-2,3-dhf: HPLC ChiraGrom, 1 hexane: i-PrOH 99:1, 0.3 mL/min, (−)-isomer t_R = 13.6 min, (+)-isomer t_R = 16.5 min; 98.7% ee, opt. rotation $[\alpha]_D = -47.2°$ *c* = 0.6 $CHCl_3$. ^{1}H NMR (300.13 MHz, $CDCl_3$): 2.59 (m, 1H), 3.14 (m, 1H), 3.94 (s, 3H, COO*Me*), 4.99 (m, 1H), 5.59 (m, 1H, H2), 6.49 (m, 1H), 7.44 (m, 2H^{ar}), 8.50 (m, 2H^{ar}). ^{13}C{^{1}H} (75.47 MHz, $CDCl_3$): 167.3 (C=O), 148.6 (C), 145.7 (C^{olefin}), 130.3 (C), 129.8 (C), 125.8 (C), 99.4 (C^{olefin}), 82.5 (C2), 52.5 (OMe), 38.3 (C3). 2-(*p*-MeOOC−C_6H_4)-2,5-dhf: HPLC ChiraGrom 2 hexane: i-PrOH 99:1, 0.3 mL/min, (−)-isomer t_R = 9.25 min, (+)-isomer t_R = 13.4 min; 93% ee, opt. rotation $[\alpha]_D = +174°$, $CDCl_3$.^{1}H NMR (300.13 MHz, $CDCl_3$): 3.93 (s, 3H, OMe), 4.75−4.95 (m, 2H), 5.8−5.9 (m, 2H), 6.05 (m, 1H), 7.38 (m, 2H^{ar}), 8.05 (m, 2H^{ar}). The same procedure using (*S*)-**1a** as ligand gave (+)-2-(*p*-MeOOC−C_6H_4)-2,3-dhf, 74 mg (42%) with 87% ee.

The arylation of 2,3-dhf using PhOTf and **1** was reported recently.[23a]

Arylation of 5-Me-2,3-dhf. $Pd(OAc)_2$ (6.7 mg, 3 mol %) and (*R*)-**1b** (61.9 mg, 6 mol %) were dissolved in 4.5 mL of benzene, and then 5-Me-2,3-dhf (456 μL, 5 mmol) was added. After 20 min, PhOTf (157 μL, 1 mmol) and EtN(i-Pr)$_2$ (510 μL, 3 mmol) were added; the solution was degassed and then stirred under Ar at 70 °C for 7 days. The reaction mixture was then treated with 200 mL of hexane and the resulting suspension filtered. The solution was washed first with 0.1 M HCl and then with 10% K_2CO_3. Drying over $MgSO_4$ was followed by solvent distillation in vacuo. The residue was chromatographed on SiO_2 using hexane/ethyl acetate, 97.5:2.5, as eluent to afford 60 mg (38%) of 2-Me-2-Ph-2,3-dhf, r_f = 0.25, and 10 mg (ca. 6%) of 2-Me-2-Ph-2,5-dhf, r_f = 0.04. For 2-Me-2-Ph-2,3-dhf, only one enantiomer was detected (NMR, Eu(hfc)$_3$, ee estimated to be >98%), opt. rotation $[a]_D = +43.1°$ *c* = 0.585 $CHCl_3$. ^{1}H NMR (300.13 MHz, $CDCl_3$, *J* in Hz): d, 1.66 (s, 3H, Me), 2.79 (ddd, 1H, H3, *J* = 15.0, 2.5, 2.5), 2.87 (ddd, 1H, H3′, *J* = 15.0, 2.5, 2.5), 4.88 (ddd, 1H, H4, *J* = 2.5, 2.5, 2.5), 6.42 (ddd, 1H, H5, *J* = 2.5, 2.5, 2.5), 7.29 (t, 1H, H^p, *J* = 7.2), 7.37 (t, 2H, H^m, *J* = 7.9), 7.44 (d, 2H, H^o, *J* = 8.0) (from NOESY: H3 cis to the methyl group). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): d, 29.5 (Me), 44.6 (C3), 87.8 (C2), 98.9 (C4), 124.8 (C^o), 127.2 (C^p), 128.7 (C^m), 144.6 (C5), 148.1 (C^i). MS (EI$^+$, *m*/*e*): 160.1 [M]$^+$, 145.1 [M − CH_3]$^+$, 77.0 [C_6H_5]$^+$. (*R*)-**1a** gives 18% yield of (+)-2-Me-2-Ph-2,3-dhf with 20% ee (NMR) and the recovery of 35% PhOTf.

Crystallography. Crystals of **3a** were mounted on an CAD4 diffractometer for the unit cell and space group determinations and for the data collection. The unit cell constants, space group determination, and the data collection for **3b** were carried out on a Siemens SMART diffractometer equipped with a CCD detector.

Structural Study of PdI(*p*-MeO_2C−C_6H_4)(1a), 3a. Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard

Table 3. Experimental Data for the X-ray Diffraction Study of Compounds PdI(*p*-MeO$_2$C−C$_6$H$_4$)(MeO−Biphep) (3a) and PdI(C$_6$F$_5$)(MeO−Biphep) (3b)

	3a	3b
formula	$C_{46}H_{39}IO_4P_2Pd$	$C_{44}H_{32}IF_5O_2P_2Pd$
mol wt	951.08	982.94
diffractometer	CAD4	SMART CCD
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1$
a, Å	10.147(4)	10.9401(5)
b, Å	19.239(9)	14.0411(7)
c, Å	11.419(6)	13.7097(7)
β, deg	91.62(4)	104.130(1)
V, Å^3	2228(2)	2042.2(2)
Z	2	2
$r_{(calcd)}$, g cm^{-3}	1.417	1.598
m, cm^{-1}	12.21	13.47
radiation	Mo Kα (graphite monochrom $\lambda = 0.710\ 69$ Å)	
θ range, deg	$2.5 < \theta < 25.0$	$1.5 < \theta < 29.4$
no. of data colld		21 699
no. of ind data	4022	9964
no. of obs reflns (n_o)	3198 [$\|F_o\| > 3.0\sigma(\|F\|)$]	8655 [$\|F_o\| > 2.0\sigma(\|F\|)$]
transmission coeff	0.7049−1.2663	0.8692−1.0000
R_{av}[a]		0.023
R (obs, reflns)	0.052	0.026
R_w, $R^2{}_w$[b]	0.068	0.051 (all data)
GOF[c]	2.518	0.879

[a] $R_{av} = \sum|F_o^2 - F_{o,av}^2|/\sum_i|F_o^2|$, $R = \sum(|F_o - (1/k)F_c|)/\sum|F_o|$. [b] $R_w = [\sum_w(F_o - (1/k)F_c)^2/\sum_w|F_o|^2]^{1/2}$ where $w = [\sigma^2(F_o)]^{-1}$; $\sigma(F_o) = [\sigma^2(F_o^2) + f^4(F_o^2)]^{1/2}/2F_o$ and $f = 0.04$. $R^2{}_w = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w|F_o^2|^2]$ where $w = [\sigma^2(F_o^2) + (aP)^2 + P]^{-1}$, $a = 0.023$ and $P = \{[F_o^2 + \max(F_o^2)]/3.0\}$. [c] GOF: (a) $[\sum_w(F_o - (1/k)F_c)^2/(n_o - n_v)]^{1/2}$; (b) $[\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

reflections were used to check the stability of the crystals and of the experimental conditions and were measured every hour. The collected intensities were corrected for Lorentz and polarization factors.[38] An empirical absorption correction[39] was also applied by using azimuthal (ψ) scans of three "high-χ" ($\chi \geq 85°$) reflections. Of the 4022 independent data collected, 3198 were considered as observed and used for the solution and refinement of the structure. Selected crystallographic and other relevant data are listed in Table 3 and in Table S1. The standard deviations on intensities were calculated in term of statistics alone, while those on F_o were calculated as shown in Table 3. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares[38] (the function minimized being $\sum[w(F_o^2 - (1/k)F_c)^2]$). 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.[40] The final full-matrix least-squares refinement cycles were carried out using anisotropic displacement parameters for the "heavy atoms" (Pd, I, and P), the aryl ligand, and the O-Me moieties of the Biphep ligand. The remaining atoms were treated isotropically. The contribution of the hydrogen atoms in calculated positions (C−H = 0.95 (Å), B(H) = 1.3 × B(C$_{bonded}$) (Å^2)) was taken into account but not refined. Upon convergence (see Table S1) no significant features were found in the Fourier difference map. The handedness of the structures was tested by refining both enantiomorphs; the coordinates giving the significantly[41] lower R_w factors were used. All calculations were carried out using the Enraf-Nonius MOLEN package.[38]

Structural Study of PdI(C$_6$F$_5$)(1a), 3b. The space group was unambiguously determined from the systematic absences, while the cell constants were refined, at the end of the data collection, using 8192 reflections ($\theta_{max} \leq 25°$) with the data reduction software SAINT,[42] developed by Siemens. The data were collected (up to sin $\theta/\lambda = 0.692$ Å^{-1}) by using ω scans, in steps of 0.3° with a sample−detector distance fixed at 50 mm. For each of the resulting 1250 "frames", counting time was 30 s. Data were corrected for Lorentz and polarization factors and empirically for absorption using the SADABS program.[43] Selected crystallographic and other relevant data are listed in Table 3 and in Table S1. The standard deviations on intensities were calculated in terms of statistics alone, while those on F_o^2 were calculated as shown in Table 3. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares,[44] minimizing the function $\sum[w(F_o^2 - (1/k)F_c^2)^2]$.

Anisotropic displacement parameters were used for all atoms. The contribution of the hydrogen atoms in their calculated positions (C−H = 0.95(Å), B(H) = 1.5 × B(C$_{bonded}$) (Å^2)) was included in the refinement using a riding model. The handedness of the structure was tested by refining the Flack parameter.[45] No extinction correction was deemed necessary. Upon convergence (see Table S1) the final Fourier difference map showed no significant peaks. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[46] All calculations were carried out by using the PC version of the SHELX-97 programs.[44]

Pd(dba)(1a). Pd$_2$(dba)$_3$·CHCl$_3$ (40 mg, 38.6 μmol) and (*S*)-MeO−Biphep (45.0 mg, 77 μmol) were dissolved in 2 mL of CH_2Cl_2 and stirred for 16 h. The orange brown solution was filtered over Celite and the filtrate evaporated to dryness in vacuo. The residue was washed with ether (6 × 1.5 mL) and the complex recrystallized from CH_2Cl_2/Et$_2$O/hexane to afford 71 mg (100%) as orange microcrystals. mp = 225 °C (dec). Anal. Calcd (found) for $C_{55}H_{46}O_3P_2Pd$ (MW = 923.3 g/mol): C, 71.55 (70.77); H, 5.02 (5.13). MS (FAB$^+$, *m/e*): 923 [M + 1]$^+$, 688 [Pd(MeO−Biphep)]$^+$. $^{31}P\{^1H\}$ NMR: (121.5 MHz, CD_2Cl_2), δ, 25.3 (b), 24.3 (b). ^1H NMR (300.13 MHz, CD_2Cl_2): δ, 3.39 (s,

(38) *MolEN: Molecular Structure Solution Procedure*; Enraf-Nonius, Delft, The Netherlands, 1990.
(39) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.
(40) *International Tables for X−ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.
(41) Hamilton, W. C. *Acta Crystallogr.* **1965**, *17*, 502.
(42) *SAINT: SAX Area Detector Integration*; Siemens Analytical Instrumentation, 1996.
(43) Sheldrick, G. M. *SADABS*; Universität Göttingen. To be published.
(44) Sheldrick, G. M *SHELX-97. Structure Solution and Refinement Package*; Universität Göttingen, 1997.
(45) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.
(46) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.

3H), 3.41 (s, 3H), 4.81 (m, b, 1H), 4.98 (m, b, 1H), 6.25 (m, 3H), 6.39 (m, 1H), 6.52 (m, 1H), 6.7−7.8 (m, 33H). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ, 55.0 (2 OMe), 68.9 (d, b, J_{PC} = 26.8 Hz), 73.6 (b), 110.5 (CH ortho to OMe), 110.7 (CH ortho to OMe), 122.0−135 (32 CH), 127−136 (10 C^i), 124.2 (b, C═C, uncoord.), 143.5 (b, C═C uncoord.), 157.9 (d, C−OMe, J_{PC} = 7.9 Hz), 158.1 (d, C−OMe, J_{PC} = 7.6 Hz), 183.01 (b, C═O). The structure of Pd(dba)(**1b**) was reported earlier. In contrast to the observations made for Pd(dba)(**1b**), there appears to be no restricted rotation around the P−C_6H_5 bonds of Pd(dba)-(**1a**), based on ^{31}P,^1H-correlation and ^1H integration measurements.

Two additional Pd(0) compexes were prepared, although not discussed.

Pd(cyclopent-4-ene-1,3-dione)(1a). $Pd_2(dba)_3$·dba (57.5 mg, 0.05 mmol) and (*S*)-MeO−Biphep (58.3 mg, 0.1 mmol) were dissolved in 2 mL of THF. To the orange-brown solution formed was added 1.2 equiv of cyclopent-4-ene-1,3-dione (11.4 mg, 0.12 mmol). The color changed to yellow. After stirring for 16 h the solution was filtered and taken to dryness in a vacuum. The residue was washed with ether (7 × 1.0 mL). The product can be recrystallized from CH_2Cl_2/Et_2O. Yield: 78 mg (99%) as yellow microcrystals, mp 265 °C (dec). Anal. Calcd (found) for $C_{43}H_{36}O_4P_2Pd$ (MW = 785.1 g/mol): C, 65.78 (65.78); H, 4.62 (4.78). MS (FAB$^+$, *m*/*e*): 785 [M + 1]$^+$, 688 [Pd-(MeOBiphep)]$^+$. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ, 28.4 (d, J = 16.8 Hz), 26.2 (d, J = 16.8 Hz).^1H NMR (400.13 MHz, CD_2Cl_2): δ, 2.33 (m, 1H), 2.80 (m, 1H), 3.44 (s, 3H), 3.47 (s, 3H), 4.36 (m, 1H), 4.80 (m, 1H), 6.28−6.36 (m, 2H), 6.51 (ddd, 1H, J = 10.4, 7.9, 1.0 Hz), 6.59 (ddd, 1H, J = 10.0, 7.9, 1.0 Hz), 6.83−7.83 (m, 22H). $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2): δ, 55.1 (OMe), 55.2 (OMe), 66.1 (CH_2), 71.3 (dd, J_{PC} = 22.4, 2.7 Hz), 73.4 (dd, J_{PC} = 22.4, 2.3 Hz), 111.0−134.9 (18 doublets, 26 CH), 127−136 (8 doublets, C^i), 158.0 (d, C−OMe, J_{PC} = 7.5 Hz), 158.1 (d, C−OMe, J_{PC} = 7.7 Hz), 200.8 (dd, C═O, J_{PC} = 4.3, 2.2 Hz), 201.9 (dd, C═O, J_{PC} = 5.0, 1.6 Hz).

Pd(benzoquinone)(1a). Synthesis was performed as for [Pd(cyclopente-4-ene-1,3-dione){(*S*)-MeO−Biphep}], but 2 equiv of benzoquinone (21.6 mg, 0.2 mmol) was employed. Yield: 52 mg (65%) as red microcrystals, mp 210 °C (dec). Anal. Calcd (found) for $C_{44}H_{36}O_4P_2Pd$ (MW = 797.1 g/mol): C, 66.3 (65.9); H, 4.55 (5.09). MS (FAB$^+$, *m*/*e*): 797 [M + 1]$^+$, 688 [Pd(MeO−Biphep)]$^+$. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ, 30.9. ^1H NMR (300.13 MHz, CD_2Cl_2): δ, 3.44 (s, 6H), 5.37 (m, 2H), 5.69 (m, 2H), 6.32 (m, b, 1H), 6.35 (m, b, 1H), 6.6 (m, 2H), 6.9 (m, 2H), 7.1−7.8 (m, 20H). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ, 55.1 (2 OMe), 104.21 (d, CH, J_{PC} = 3.5 Hz), 104.26 (d, CH, J_{PC} = 3.5 Hz), 105.26 (d, CH, J_{PC} = 3.5 Hz), 105.31 (d, CH, J_{PC} = 3.5 Hz), 111.3−135.2 (12 doublets, 3 broad signals, 26 CH), 127.5−135.5 (8 doublets, C^i), 158.06 (d, C−OMe, J_{PC} = 5.2 Hz), 158.14 (d, C−OMe, J_{PC} = 5.2 Hz), 185.2 (d, C═O, J_{PC} = 3 Hz), 185.24 (d, C═O, J_{PC} = 3 Hz).

PdI(MeOOC−C_6H_4)(1a), 3a. (*S*)-MeO−Biphep (58.3 mg, 0.1 mmol) and [PdI(TMEDA)(MeOOC−C_6H_4)] (48.5 mg, 0.1 mmol) were dissolved in 5 mL of THF and stirred at 40 °C for 14 h. The solution was filtered and taken to dryness. The residue was washed with Et_2O (5 × 2 mL) and the crude yellow product recrystallyzed from CH_2Cl_2 and Et_2O (1 mL CH_2Cl_2 condensed into the Schlenk tube and layered with Et_2O). Over a period of 24 h crystals were formed, which were washed with Et_2O and dried in a vacuum. Yield: 72.7 mg (76.4%) of yellow crystals, mp 160 °C (dec). Anal. Calcd (found) for $C_{46}H_{39}O_4P_2$-PdI (MW = 951.1 g/mol) C, 58.09 (57.81); H, 4.13 (4.31). MS (FAB$^+$, *m*/*e*): 823.0 [Pd(C_6H_4COOMe)(MeO−Biphep)]$^+$, 814.9 [PdI(MeO−Biphep)]$^+$. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ, 10.1 (J = 42.7 Hz), 21.5 (J = 42.7 Hz). ^1H NMR (300 MHz, CD_2Cl_2): δ, 3.34 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.79 (s, 3H, $COOCH_3$), 6.36−6.41 (m, 2H), 6.44−6.51 (m, 1H), 6.8−6.9 (m, 1H), 7.0−7.1 (m, 2H), 7.11−7.8 (m, 24H). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ, 51.7 (COOMe), 55.0 (OMe), 55.3 (OMe), 111.2 (d, J_{PC} = 1.6 Hz), 112.2 (d, J_{PC} = 1.6 Hz), 124.6 (C4), 126.8 (dd, C3, J_{PC} = 8.7, 4.6 Hz), 123.7−137.2 (16 doublets, 24 CH), 126.5−134.5 (8 doublets, 8 C^i), 138.7 (dd, C2, J_{PC} = 4.8, 1.6 Hz), 157.8 (d, C−OMe, J_{PC} = 9.7 Hz), 158.3 (d, C−OMe, J_{PC} = 10.6 Hz), 167.2 (dd, C1, J_{PC} = 128.0, 6.0 Hz) 168.2 (C═O).

PdI(C_6F_5)(1a) 3b. Reaction conditions as in **3a**: THF, 60 °C, 96 h. Yield: 50 mg (51%) as orange brown crystals from CH_2Cl_2 /Et_2O/hexane. Mp: 260−265 °C (dec). Anal. Calcd (found) for $C_{44}H_{32}F_5O_2P_2PdI$ (MW = 983.0 g/mol): C, 53.76 (53.70); H, 3.28 (3.45). MS (FAB$^+$, *m*/*e*): 855 [M − I]$^+$, 815 [M − C_6F_5]$^+$, 688.1 [Pd(MeO−Biphep)]$^+$. ^{31}P NMR (121.5 MHz, THF): δ, 20.9 (m (8 line multiplet)), 13.4 (m (ca. 15 lines)). ^1H NMR (300 MHz, CD_2Cl_2): δ, 3.39 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 6.4−6.5 (m, 3H), 6.84 (m, 1H), 7.1−7.4 (m, 9H), 7.46 (m, 1H), 7.5−7.58 (m, 3H), 7.6−7.8 (m, 5H). $^{13}C-^{19}F$ HMQC: δ, 122.1 (d, C1, J_{PC} = 118 Hz), 136.0/136.7 (C3/C5), 137.9 (C4), 145.0/145.7 (C2/C6). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ, 55.0 (OMe), 55.4 (OMe), 112.3 (d, J_{PC} = 2 Hz), 112.9 (d, J_{PC} = 2 Hz), 124.4 (dd, CH, J_{PC} = 11.0, 3.0 Hz), 125.3−137.8 (13 doublets, 19 CH), 126−134 (8 doublets, 8 C^i), 157.9 (d, C−OMe, J_{PC} = 10 Hz), 158.3 (d, C−OMe, J_{PC} = 11 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ, −113.5 (m, 1F), −115.4 (m, 1F), −163.1 (t, 1F, J = 20), −164.2 (m, 1F), −165.2 (m, 1F). The complexity arises from ^2J(P,P) plus ^{19}F spin−spin coupling.

PdBr(C_6F_5)(1a). Reaction conditions as in **3a**: THF, 60 °C, 96 h. Yield: 48.8 mg (52%) as orange crystals from CH_2Cl_2 /Et_2O/hexane. Mp; 275 °C (dec). Anal. Calcd (found) for $C_{44}H_{32}F_5O_2P_2PdBr$ (MW = 936.0 g/mol): C, 56.46 (56.51); H, 3.44 (3.69). MS (FAB$^+$, *m*/*e*): 855 [M − Br]$^+$, 769.0 [M − C_6F_5]$^+$, 688.1 [Pd(MeO−Biphep)]$^+$. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ, 27.45 (8 line multiplet, J_{PP} ca. 29 Hz), 15.7 (ca. 15 line multiplet, J_{PP} ca. 29 Hz). ^1H NMR (300 MHz, CD_2Cl_2): δ, 3.39 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 6.33−6.5 (m, 3H), 6.85 (td, 1H, J = 8.1, 2.3 Hz), 7.09−7.34 (m, 9H), 7.41−7.55 (m, 4H), 7.62 (dd, 1H, J = 11.5, 8.0 Hz), 7.65−7.74 (m, 2H), 7.76−7.86 (m, 2H). $^{13}C-^{19}F$ HMQC δ, 126.7 (d, C1, J_{PC} = 133 Hz), 135.9/136.8 (C3/C5), 137.8 (C4), 145.2/146.0 (C2/C6). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ, 55.1 (OMe), 55.4 (OMe), 112.5 (d, J_{PC} = 2.6 Hz), 112.9 (d, J_{PC} = 2.6 Hz), 124.4 (dd, CH, J_{PC} = 10.6, 3.0 Hz), 125.1−137 (13 doublets, 19 CH), 126−134 (8 doublets, 8 C^i), 157.9 (d, C−OMe, J_{PC} = 10.4 Hz), 158.4 (d, C−OMe, J_{PC} = 11.3 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ, −115.6 (m, 1F), −116.5 (m, 1F), −163.1 (t, 1F, J = 20), −164.0 (m, 1F), −165.83 (m, 1F). The complexity arises from ^2J(P,P) plus ^{19}F spin−spin coupling.

PdBr(4-cyanophenyl)(1a). This was prepared as described for **3a**. Reaction conditions: THF, 40 °C, 14 h. Yield: 60 mg (69%) as yellow crystals from CH_2Cl_2/Et_2O. Mp: 173 °C (dec). Anal. Calcd (found) for $C_{45}H_{36}NO_2P_2PdBr$ (MW = 871.1 g/mol): C, 62.05 (61.78); H, 4.17 (4.35); N, 1.61 (1.62). MS (FAB$^+$, *m*/*e*) 790 [M − Br]$^+$, 769.0 [M − C_6H_4CN]$^+$, 688.1 [Pd(MeO−Biphep)]$^+$. ^{31}P NMR (121.5 MHz, THF): δ, 12.4 (d, J = 41.4 Hz), 26.9 (d, J = 41.4 Hz). ^1H NMR (400.13 MHz, CD_2Cl_2): δ, 3.38 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 6.36−6.47 (m, 3H), 6.88 (td, 1H, J = 8.2, 2.2 Hz), 6.96 (m, 2H, H3), 7.05−7.37 (m, 12H), 7.43 (m, 1H), 7.47−7.52 (m, 3H), 7.57 (m, 2H, H2), 7.64−7.72 (m, 2H), 7.74−7.85 (m, 4H). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ, 55.1 (OMe), 55.3 (OMe), 105.9 (d, C4, J_{PC} = 1.6 Hz), 112.16 (d, J_{PC} = 2.5 Hz), 112.3 (d, J_{PC} = 1.6 Hz), 120.5 (d, C≡N, J_{PC} = 0.7 Hz), 123.6−136.6 (16 doublets, 24 CH), 126.7−133.5 (8 doublets, 8 C^i), 129.2 (dd, C3, J_{PC} = 8.9, 1.8 Hz), 138.4 (dd, C2, J_{PC} = 5.0, 1.8 Hz), 157.8 (d, C−OMe, J_{PC} = 10 Hz), 158.4 (d, C−OMe, J_{PC} = 11 Hz), 172.0 (dd, C1, J_{PC} = 132.7, 4.1 Hz).

Borohydride Route to PdBr(4-cyanophenyl)(1a). $NaBH_4$ and $LiBHEt_3$ have been recently used to prepare zerovalent complexes.[47,48] $NaBH_4$ (3.8 mg, 0.1 mmol) was added to a

(47) Wicht, D. K.; Zhuravel, M. A.; Gregush, R. V.; Glueck, D. S.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **1998**, *17*, 1412−1419.

suspension of [$PdCl_2$\{(*S*)-MeO−Biphep\}] (38 mg, 50 μmol) in acetone at −50 °C. There was an immediate color change from yellow to red-orange. The mixture was slowly warmed to room temperature and 4-bromo-benzonitrile (10 mg, 55 μmol) added. The suspension became light yellow within 1 h. Filtration, distillation in vacuo of the solvent, and recrystallization of the residue from CH_2Cl_2/Et_2O gave 30.4 mg (70%) of the pure title compound. Analytical data are almost identical to those given above.

PdBr(*p*-nitrophenyl)(1a). This was prepared as in **3a** except that the mixture was refluxed for 2 h in THF. The product (28.5 mg, 32%) was obtained from CH_2Cl_2/hexane, mp 165 °C (dec). Anal. Calcd (found) for $C_{44}H_{36}NO_4P_2PdBr$ (MW = 891.0 g/mol): C, 59.31 (59.05); H, 4.07 (4.10); N, 1.57 (1.66). MS (FAB$^+$, *m*/*e*): 810.2 [M − Br]$^+$, 769.0 [M − $C_6H_4NO_2$]$^+$, 688.1 [Pd(MeO−Biphep)]$^+$. ^{31}P NMR (121.5 MHz, THF): δ, 12.5 (d, J ca. 41 Hz), 26.6 (d, ca. 41 Hz). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ, 3.40 (s, 3H), 3.49 (s, 3H), 6.35−6.5 (m, 3H), 6.89 (m, 1H), 7.0−8.0 (m, 26H). ^{13}C\{^{1}H\} NMR (75.47 MHz, CD_2Cl_2): δ, 55.15 (OMe), 55.30 (OMe), 112.27 (d, J_{PC} = 2.3 Hz), 112.36 (d, J_{PC} = 1.8 Hz), 120.32 (dd, C3, J_{PC} = 9.1, 1.8 Hz), 123.7−136.4 (16 doublets, 24 CH), 120−136.7 (8 doublets, 8 C^i), 137.9 (dd, C2, J_{PC} = 4.6, 1.8 Hz), 144.5 (C4), 157.8 (d, C−OMe, J_{PC} = 10.5 Hz), 158.4 (d, C−OMe, J_{PC} = 11.3 Hz), 176.7 (dd, C1, J_{PC} = 133.0, 4.0 Hz).

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Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for **3a** and **3b**, including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, bond distances and angles, and ORTEP figures showing the full numbering schemes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980783L

(48) Hodgson, M.; Parker, D.; Taylor, R. J.; Feruson, G. *Organometallics* **1988**, *7*, 1761−1766.