$Os(Et_2dtc)_3$ was found to be slightly greater than that of $Ru(Et_2dtc)_3$.[32] The difference in the stereodynamic properties between $Ru(DBQ)_3$ and $Os(DBQ)_3$ is more dramatic, however. Similarities in b/l ratio and twist angle, structural features that should be sensitive to transition-state energy for intramolecular rearrangement, indicate that the difference in fluxional character results from a ligand field effect. Even though infrared spectra fail to detect a difference in electronic structure, the M–O and C–O lengths obtained from the four structure determinations point to a higher charge for the metal of $Os(DBQ)_3$. While there is a clear difference in electron distribution for metals of adjacent groups, there appears to also be a difference in metal charge for the three members of the iron triad.

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Supplementary Material Available: Tables containing details of the structure determinations on *cis*-$Ru(DBQ)_3$, *trans*-$Ru(DBQ)_3$, and *trans*-$Os(DBQ)_3$, anisotropic thermal parameters for the atoms of all three structures, complete lists of bond distances and angles, and hydrogen atom locations (27 pages). Ordering information is given on any current masthead page.

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(32) Given, K. W.; Wheeler, S. H.; Jick, B. S.; Maheu, L. J.; Pignolet, L. H. *Inorg. Chem.* **1979**, *18*, 1261.

Alkylnickel and -palladium Alkoxides Associated with Alcohols through Hydrogen Bonding

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Abstract: *trans*-PdR_2L_2 (R = CH_3, C_2H_5; L = PMe_3, PEt_3) and *trans*-$NiMe_2(PMe_3)_2$ react with 2 equiv of fluorinated alcohols and para-substituted phenols to give complexes formulated as *trans*-$PdR(OR')(HOR')L_2$ (R' = $CH(CF_3)Ph$, C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-FC_6H_4) and *trans*-$NiMe(OR')(HOR')(PMe_3)_2$ (R' = $CH(CF_3)Ph$, C_6H_5), respectively. IR and NMR spectra of these complexes indicate the presence of strong O–H···O hydrogen bonding between the alkoxide (or aryloxide) ligand and the alcohol (or substituted and nonsubstituted phenol) both in the solid state and in solution. X-ray crystallography of *trans*-$PdMe(OPh)(HOPh)(PMe_3)_2$ and *trans*-$NiMe(OPh)(HOPh)(PMe_3)_2$ shows that the phenoxide oxygen in each complex is associated with phenol through hydrogen bonding. Reactions of *trans*-$PdMe_2(PMe_3)_2$ with equimolar substituted and nonsubstituted phenols, respectively, give *trans*-$PdMe(OC_6H_4$-*p*-$X)(PMe_3)_2$ (X = H, Me, OMe, F, Cl, Br), which react with additional equimolar phenols to give phenol-bonded palladium complexes *trans*-$PdMe(OC_6H_4$-*p*-$X)(HOC_6H_4$-*p*-$X)(PMe_3)_2$. *trans*-$PdMe(OPh)(PMe_3)_2$ reacts also with fluorinated alcohols to give *trans*-$PdMe(OPh)(HOCH(CF_3)Ph)(PMe_3)_2$ and *trans*-$PdMe(OPh)(HOCH(CF_3)_2)(PMe_3)_2$, which are fully characterized by means of IR and NMR spectroscopy and X-ray crystallography. ^1H NMR spectra of mixtures of phenol with *cis*-$PdMe_2(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane) and *cis*-$PdMe_2(dpe)$ (dpe = 1,2-bis(diphenylphosphino)ethane) indicate formation of strong O–H···O hydrogen bonding between phenol and the phenoxide ligand in solution. Equilibrium constants for the association of phenol with the palladium phenoxide having dmpe ligand, obtained by means of ^1H NMR spectroscopy, are smaller than those of *trans*-$PdMe(OPh)(PMe_3)_2$ with phenol. NMR spectra of *trans*-$PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$ and *trans*-$PdMe(OAr)(HOAr)(PMe_3)_2$ at variable temperatures (−60 to +40 °C) indicate the presence of intramolecular alkoxide-exchange process between the alkoxide ligand and the alcohol moiety on the NMR time scale. Addition of phenol to *trans*-$PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$ causes displacement of the alkoxide ligand by phenoxide group to give *trans*-$PdMe(OPh)(HOCH(CF_3)Ph)(PMe_3)_2$. Reactions of *trans*-$PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$ and *trans*-$PdMe(OPh)(HOCH(CF_3)Ph)(PMe_3)_2$ with CO give $MeCOOCH(CF_3)Ph$ in 99% and 46% yields, respectively. Reactions of *trans*-$PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$ with aryl esters give methylpalladium aryloxide complexes and esters of the fluorinated alcohol through exchange of the alkoxide group between the complex and the ester. The alkoxide (phenoxide) complexes catalyze transesterification of alcohols with esters. Mechanistic implications of the present results regarding the transesterification are presented.

Late-transition-metal alkoxides[3-11] are regarded as important intermediates in various transition-metal-catalyzed synthetic organic reactions. Those of platinum and iridium have recently attracted considerable attention. Chemical properties of these metal alkoxides regarding β-hydrogen elimination of the alkoxide

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(1) Research Laboratory of Resources Utilization.

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(3) (a) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3028. (b) Bennett, M. A.; Yoshida, T. *Ibid.* **1978**, *100*, 1750.

(4) Lehmkuhl, H.; Eisenbach, W. *Ann.* **1975**, 672.

(5) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.

(6) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239.

(7) (a) Komiya, S.; Tane-ichi, S.; Yamamoto, A.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 673. (b) Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 1363.

(8) (a) Arthur, T.; Robertson, D. R.; Tocher, D. A.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 389. (b) Gould, R. O.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1984**, *263*, 375.

(9) (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (b) Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 977. (c) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686. (d) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805.

(10) (a) Oro, L. A.; Carmona, D.; Lamata, M. P.; Apreda, M. C.; Foces-Foces, C.; Cano, F. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1823. (b) Lehoz, F. J.; Oro, L. A.; Lamata, M. P.; Puebla, M. P.; Foces-Foces, C.; Cano, F. A. *J. Organomet. Chem.* **1986**, *316*, 221.

(11) (a) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179. (b) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Ibid.* **1986**, *5*, 390. (c) Bernard, K. A.; Atwood, J. D. *Ibid.* **1987**, *6*, 1133. (d) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thomson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939.

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ligand to release aldehydes or ketones[9d,11b,12] and insertion of CO into the metal–alkoxide bond to give alkoxycarbonyl complexes have been examined.[3b,9b,c,11a] By comparison, reports on detailed studies on preparation and chemical properties of nickel and palladium alkoxides are still rare,[5] although these alkoxides are postulated to play important roles in synthetic organic reactions catalyzed by these metals.[13-15]

Metal alkoxides are often used as promoters of transesterification[16,17] and hydrogen transfer from alcohols to ketones.[18,19] These reactions possibly involve associative exchange of alcohol with the alkoxide ligand. However, there have been no reports about association of an alcohol with a late-transition-metal alkoxide until quite recently.

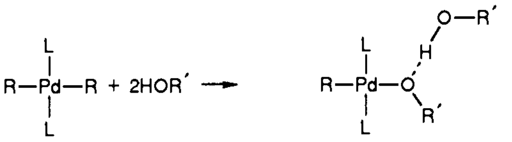
While the present work was in progress, Bergman, Braga, and their respective co-workers reported isolation of rhodium and palladium alkoxides and aryloxides associated with alcohol (or phenol) through strong O–H···O hydrogen bonding that was established by X-ray analysis.[20,21] The rhodium aryloxides having substituted phenols showed strong hydrogen bonding also in solution as was determined by detailed NMR studies and calorimetric measurements.[20] In the course of our studies on alkylnickel and -palladium complexes having fluorinated alkoxides,[22] we have also observed hydrogen bond formation of these alkoxides and aryloxides with alcohols and phenols, respectively.

We report here full details of our study on synthesis, characterization, and properties of these metal alkoxides and their adducts with alcohols and phenols. Association equilibria of these alkoxides with alcohols have been studied and their solution properties involving exchange of the alkoxide ligand with alcohols examined. Also discussed here are carbonylation of these alkylmetal alkoxides to give carboxylic esters and exchange reactions of the alkoxide ligand in the palladium alkoxide complexes with aryloxide and aryl sulfide groups in carboxylic and carbothioic esters, respectively, through transesterification.

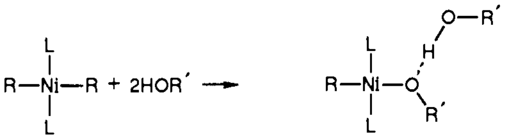
Results and Discussion

Preparation of Alkylnickel and -palladium Alkoxides (or Aryloxides) Having Hydrogen-Bonded Alcohols (or Phenols). *trans*-$PdMe_2(PMe_3)_2$ and *trans*-$PdEt_2(PMe_3)_2$ react smoothly with 2 equiv of 2,2,2-trifluoro-1-phenylethanol below 0 °C to give alkylpalladium alkoxides, $PdR(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$: **1**, R = Me; **2**, R = Et. The weaker acid methanol does not react with these dialkylpalladium complexes. Low electric conductivity of an acetone solution of **1** suggests its nonionic structure. Thermolyses of **1** in the solid state and in solution give methane and the alcohol as major products but do not give trifluoroacetophenone, which is expected as a product of β-hydrogen elimination of the alkoxide ligand, similar to our observation in thermolysis of $PdMe(OCH(CF_3)Ph)(dpe)$ without associated alcohol.[22]

Reactions of various para-substituted phenols with *trans*-PdR_2L_2 (R = Me, Et; L = PMe_3, PEt_3) also give aryloxide complexes having hydrogen-bonded phenols $PdR(OC_6H$-*p*-$X)(HOC_6H_4$-*p*-$X)L_2$ (X = H, Me, OMe, F, Cl, Br) (**3**–**10**) in moderate to good yields, respectively. Similar reactions of *trans*-$NiMe_2(PMe_3)_2$ with 2 equiv of 2,2,2-trifluoro-1-phenylethanol and phenol also give nickel alkoxide and phenoxide having hydrogen-bonded alcohol and phenol, respectively. Palladium complexes **1**–**10** are obtained as colorless crystals that are stable in the air for several minutes, while the orange crystals of nickel complexes **11** and **12** are extremely sensitive to oxygen and moisture. Complexes **1**–**12** have strong O–H···O hydrogen bonding between the alkoxide (or aryloxide) ligand and the associated alcohol (or phenol) both in the solid state and in solution. The presence of the hydrogen bonding in these complexes has been unambiguously established by means of X-ray crystallography and IR and NMR spectroscopy. Their detailed features are shown later.

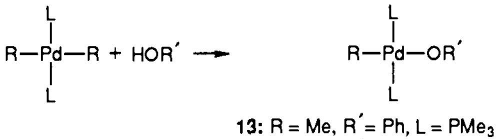

(1)

1: R = Me, R′ = $CH(CF_3)Ph$, L = PMe_3
2: R = Et, R′ = $CH(CF_3)Ph$, L = PMe_3
3: R = Me, R′ = Ph, L = PMe_3
4: R = Me, R′ = C_6H_4-*p*-Me, L = PMe_3
5: R = Me, R′ = C_6H_4-*p*-OMe, L = PMe_3
6: R = Me, R′ = C_6H_4-*p*-F, L = PMe_3
7: R = Me, R′ = C_6H_4-*p*-Cl, L = PMe_3
8: R = Me, R′ = C_6H_4-*p*-Br, L = PMe_3
9: R = Me, R′ = Ph, L = PEt_3
10: R = Et, R′ = Ph, L = PMe_3


(2)

11: R = Me, R′ = $CH(CF_3)Ph$, L = PMe_3
12: R = Me, R′ = Ph, L = PMe_3

When reactions of *trans*-$PdMe_2(PMe_3)_2$ with *equimolar* amounts of phenol or para-substituted phenols were performed, complexes without associated phenols were obtained, similar to reactions of *trans*-$PdMe_2(PEt_3)_2$ with equimolar amounts of phenols, giving *trans*-$PdMe(OAr)(PEt_3)_2$.[23] Palladium dimethyl complexes having chelating bidentate ligands such as dpe (dpe = 1,2-bis(diphenylphosphino)ethane) and dmpe (dmpe = 1,2-


(3)

13: R = Me, R′ = Ph, L = PMe_3
14: R = Me, R′ = C_6H_4-*p*-Me, L = PMe_3
15: R = Me, R′ = C_6H_4-*p*-OMe, L = PMe_3
16: R = Me, R′ = C_6H_4-*p*-F, L = PMe_3
17: R = Me, R′ = C_6H_4-*p*-Cl, L = PMe_3
18: R = Me, R′ = C_6H_4-*p*-Br, L = PMe_3
19: R = Me, R′ = C_6H_4-*p*-CN, L = PMe_3

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(12) Goldman, A. S.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 7537.

(13) (a) Tamaru, Y.; Inoue, K.; Yamada, Y.; Yoshida, Z. *Tetrahedron Lett.* **1981**, 1801. (b) Tamaru, Y.; Yamada, Y.; Inoue, K.; Yamamoto, Y.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 1286.

(14) (a) Nagashima, H.; Tsuji, J. *Chem. Lett.* **1981**, 1171. (b) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140. (c) Tsuji, J.; Yamada, T.; Minami, I.; Nisar, M. *J. Org. Chem.* **1987**, *52*, 2988.

(15) (a) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1975; Vol. 2, p 294. (b) Davies, S. G.; *Organotransition Metal Chemistry: Application to Organic Synthesis*; Pergamon: Oxford, 1982; p 348. (c) Jolly, P. W. *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 773. (d) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic: New York, 1985; p 341. (e) Garziani, M.; Ugualiati, P.; Carturan, G. *J. Organomet. Chem.* **1971**, *27*, 275. (f) Murahashi, S.-I.; Mitsue, Y.; Ike, K. *J. Chem. Soc., Chem. Commun.* **1987**, 125. (g) Morris, G.; Oakley, D.; Pippard, D. A.; Smith, D. J. H. *Ibid.* **1987**, 410, and references therein. (h) Alper, H.; Vasapollo, G.; Hartstock, F. W.; Mlekuz, M.; Smith, D. J. H.; Morris, G. E. *Organometallics* **1987**, *6*, 2391.

(16) (a) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic: New York, 1968; Vol. I, Chapter 10, and references therein. (b) Otera, J.; Yano, T.; Kawabata, A.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 2383.

(17) Kubota, M.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 146.

(18) Henbest, H. B.; Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 601 and 604.

(19) Camus, A.; Mestroni, G.; Zassinovich, G. *J. Mol. Catal.* **1979**, *6*, 231.

(20) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563.

(21) Braga, D.; Sabatino, P.; Bugno, C. D.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, *334*, C46.

(22) (a) Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (b) Kim, Y.-J.; Osakada, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 964.

(23) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.

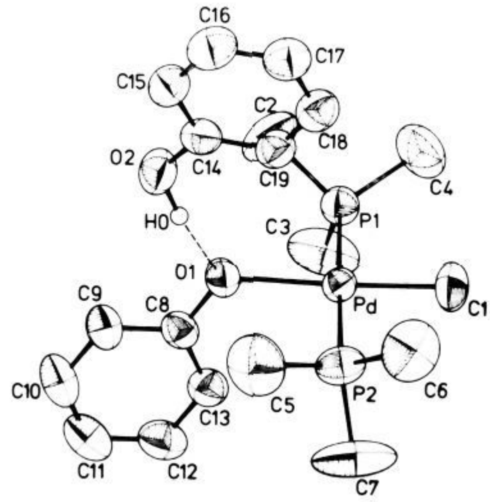
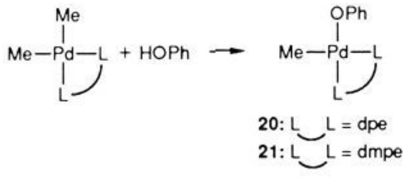


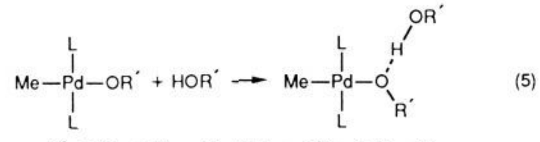
Figure 1. ORTEP diagram of *trans*-PdMe(OPh)(HOPh)(PMe$_3$)$_2$ (**3**) showing 50% probability thermal motion ellipsoid.

bis(dimethylphosphino)ethane) react with equimolar amounts of phenol to give PdMe(OPh)(dpe) (**20**) and PdMe(OPh)(dmpe) (**21**), respectively.


$$\mathrm{Me{-}PdMe(L{\frown}L)} + \mathrm{HOPh} \longrightarrow \mathrm{Me{-}Pd(OPh)(L{\frown}L)} \qquad (4)$$

20: L⌣L = dpe
21: L⌣L = dmpe

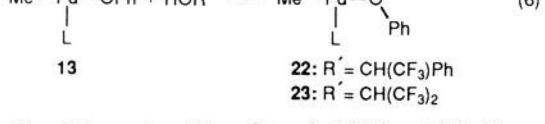
The isolated alkylpalladium phenoxide complexes **13**–**18** react further with an equimolar amount of substituted and nonsubstituted phenols to give complexes having O–H···O hydrogen bonding between phenol (or substituted phenol) and the aryloxide ligand.


$$\mathrm{Me{-}PdL_2{-}OR'} + \mathrm{HOR'} \longrightarrow \mathrm{Me{-}PdL_2{-}O(R')\cdots H{-}OR'} \qquad (5)$$

R$'$ = C_6H_5, C_6H_4-*p*-Me, C_6H_4-*p*-OMe, C_6H_4-*p*-F, C_6H_4-*p*-Cl, C_6H_4-*p*-Br; L = PMe$_3$

p-Cyanophenol is exceptional in eq 5, and addition of an excess of *p*-cyanophenol to a solution of methylpalladium cyanophenoxide complex did not lead to formation of the hydrogen-bonded adduct, probably due to lack of sufficient electron density on the oxygen atom in the *p*-cyanophenoxide ligand in **19** to form hydrogen bonding.

The phenol-free methylpalladium phenoxide complex **13** reacts with fluorinated alcohols such as 2,2,2-trifluoro-1-phenylethanol and 1,1,1,3,3-hexafluoro-2-propanol to give complexes PdMe(OPh)(HOCH(CF$_3$)Ph)(PMe$_3$)$_2$ (**22**) and PdMe(OPh)(HOCH(CF$_3$)$_2$)(PMe$_3$)$_2$ (**23**), respectively. These complexes also show strong O–H···O hydrogen bonding between the phenoxide ligand and fluorinated alcohols.


$$\mathrm{Me{-}PdL_2{-}OPh} + \mathrm{HOR'} \longrightarrow \mathrm{Me{-}PdL_2{-}O(Ph)\cdots H{-}O{-}R'} \qquad (6)$$

13

22: R$'$ = CH(CF$_3$)Ph
23: R$'$ = CH(CF$_3$)$_2$

X-ray Crystallography of Complexes 3, 12, 13, and 22. X-ray crystallography revealed the molecular structures of complexes **3**, **12**, and **22** as having hydrogen-bonded alcohol or phenol and **13** without the associated phenol. Crystal data and selected bond lengths and angles are summarized in Tables I and II, respectively. Molecular structures of the complexes are shown in Figures 1–4. These complexes have slightly distorted square-planar coordination around palladium and nickel. The methyl carbon atoms of the PMe$_3$ ligands with respect to the P–Pd–P axis are eclipsed in **3**, **12**, and **22**, whereas in **13** they are staggered. The phenyl plane of the phenoxide ligand in **3**, **12**, **13**, and **22** is nearly perpendicular to the coordination plane. Palladium complex **3** and its nickel analogue **12** have similar unit cell constants and similar positions of the metal atoms in the unit cells. Molecular structures of these two complexes are quite similar except for distances between coordination atoms (C, O, P) and metal centers, indicating that **3** is isomorphous with **12**.

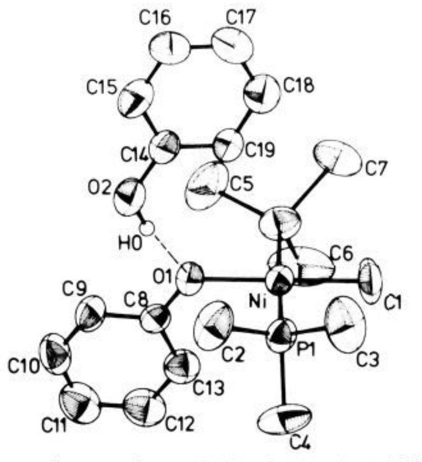


Figure 2. ORTEP diagram of *trans*-NiMe(OPh)(HOPh)(PMe$_3$)$_2$ (**12**) showing 50% probability thermal motion ellipsoid.

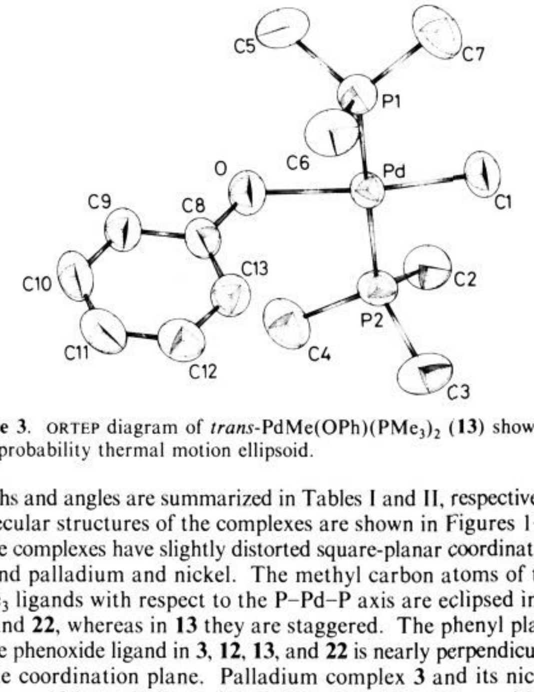


Figure 3. ORTEP diagram of *trans*-PdMe(OPh)(PMe$_3$)$_2$ (**13**) showing 50% probability thermal motion ellipsoid.

Complexes **3**, **12**, and **22** have a phenol or 2,2,2-trifluoro-1-phenylethanol moiety that is associated with the phenoxide ligand through O–H···O hydrogen bonding. Distances between the oxygen of the associated alcohol or phenol and that of the phenoxide ligand are in the range 2.59–2.61 Å. The OH hydrogen atoms were located in difference Fourier maps at distances of 1.61–1.62 Å from the oxygen atom of the phenoxide ligand and at distances of 1.00–1.01 Å from that of the associated phenol and alcohol. The O–H···O angles in these complexes are in the range 165–170°, indicating that the hydrogen is close to the line connecting two oxygen atoms. Distances and angles characteristic of O–H···O hydrogen-bonding systems in organic compounds have been reviewed,[24a,25a] and a relationship between their O···O, O–H, and

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(24) *The Hydrogen Bond. II. Structure and Spectroscopy*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976. (a) Olovsson, I.; Jonsson, P.-G. *X-Ray and Neutron Diffraction Studies of Hydrogen Bonding System*; North-Holland: Amsterdam; p 393; (b) Tucker, E. E.; Lippert, E. *High Resolution Nuclear Magnetic Resonance Studies of Hydrogen Bonding*; North-Holland: Amsterdam; p 791.

Table I. Crystal Data and Details of the Structure Determination of Complexes **3**, **12**, **13**, and **22**

	3	**12**	**13**	**22**
		Crystal Data		
formula	$C_{19}H_{32}O_2P_2Pd$	$C_{19}H_{32}O_2P_2Ni$	$C_{13}H_{26}OPPd$	$C_{21}H_{33}O_2P_2F_3Pd$
mol wt	460.61	412.91	335.54	542.63
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
crystal system	monoclinic	monoclinic	monoclinic	triclinic
a (Å)	25.720 (4)	26.123 (6)	12.7895 (9)	10.776 (9)
b (Å)	9.221 (1)	8.901 (3)	11.3242 (6)	13.810 (13)
c (Å)	9.690 (2)	9.641 (4)	11.5761 (11)	8.981 (10)
α (deg)				99.71 (9)
β (deg)	98.95 (1)	98.98 (3)	92.78 (1)	93.12 (1)
γ (deg)				96.01 (8)
V (Å^3)	2243.0 (6)	2214.3 (1.0)	1674.6 (2)	1306.5 (2.3)
Z	4	4	4	2
d_{calcd}[e]	1.365	1.239	1.455	1.380
d_{obsd}	1.347	b	1.415	c
$F(000)$	952	880	692	556
μ (cm^{-1}) (for Mo Kα)	9.64	10.29	11.71	8.54
crystal size (mm)	0.15 × 0.15 × 0.35	0.10 × 0.20 × 0.25	0.20 × 0.20 × 0.25	0.25 × 0.25 × 0.40
		Data Collection and Refinement		
radiation	MoKα	MoKα	MoKα	MoKα
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan rate (deg/min)	8	8	8	8
hkl	$-33 < h < 33$	$-30 < h < 30$	$-16 < h < 16$	$-12 < h < 12$
	$0 < k < 11$	$0 < k < 10$	$0 < k < 11$	$-16 < k < 16$
	$0 < l < 12$	$0 < l < 11$	$0 < l < 15$	$0 < l < 10$
2θ range, deg	3.0–60.0	3.0–50.0	3.0–55.0	3.0–50.0
no. of reflctns used ($\lvert F_o\rvert > 3\sigma(F_o)$)	4257	2374	2941	4054
q^d	0.015	0.034	0.009	0.015
R^e	0.042	0.076	0.038	0.037
R_w^f	0.041	0.077	0.038	0.039

[a] By flotation in a CCl_4–hexane mixture. [b] Not measured due to decomposition of the complex by halogenated solvents. [c] Not measured due to good solubility of **13** to halogenated solvents. [d] Weighting scheme has the form of $w = 1/[\sigma(F_o)^2 + (qF_o)^2]$, where $\sigma(F_o)$ is esd by counting statics. [e] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [f] $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$.

Table II. Selected Bond Distances (Å) and Angles (deg)[a]

	3	**12**	**13**	**22**
		Distances		
M–C1	2.044 (5)	1.95 (1)	2.039 (4)	2.043 (5)
M–O1	2.134 (3)	1.932 (5)	2.106 (3)	2.107 (2)
M–P1	2.293 (1)	2.192 (2)	2.298 (1)	2.301 (1)
M–P2	2.304 (1)	2.195 (3)	2.286 (1)	2.299 (1)
O1–C8	1.339 (5)	1.331 (9)	1.320 (5)	1.320 (4)
O1···O2	2.593 (4)	2.602 (8)		2.601 (4)
O1···HO	1.61	1.61		1.62
O2–HO	1.00	1.01		1.00
		Angles		
C1–M–P1	89.9 (2)	88.6 (2)	88.2 (1)	88.4 (2)
C1–M–P2	88.9 (2)	89.4 (3)	91.8 (1)	90.9 (2)
C1–M–O1	176.8 (1)	177.8 (3)	172.8 (2	177.2 (2)
P1–M–P2	178.53 (5)	177.8 (1)	178.27 (5)	177.76 (5)
P1–M–O1	89.02 (8)	89.5 (2)	93.48 (9)	91.31 (7)
P2–M–O1	92.28 (9)	92.5 (2)	86.61 (9)	89.50 (7)
M–O1–C8	121.4 (2)	121.9 (5)	127.1 (3)	124.4 (2)
M–O1–O2	120.5 (1)	121.2 (3)		105.6 (1)
O1···HO–O2	169.9	165.6		165.4

[a] M = Ni for **12** and M = Pd for **3**, **13**, and **22**. Standard deviations are in parentheses.

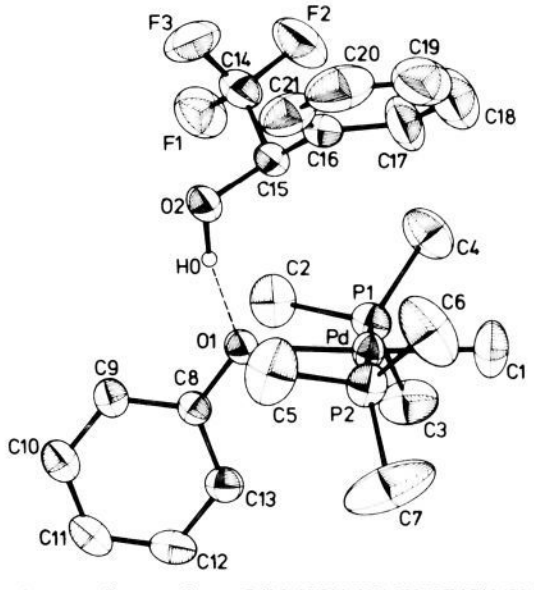

Figure 4. ORTEP diagram of *trans*-$PdMe(OPh)(HOCH(CF_3)Ph)(PMe_3)_2$ (**22**) showing 50% probability thermal motion ellipsoid.

O···H distances has been formulated. The bond lengths of our compounds seem reasonable by comparison with those in the above literature. Previous reports of $Rh(OC_6H_4\text{-}p\text{-}Me)(HOC_6H_4\text{-}p\text{-}Me)(HOC_6H_4\text{-}p\text{-}Me)(PMe_3)_3$ and $PdH(OPh)(HOPh)(P(C_6H_{11})_3)_2$ showed O···O distances of 2.62 and 2.59 Å, respectively, and showed elongated O–H bond distances (about 1.2 Å) and somewhat short O···H distances (1.4 and 1.57 Å, respectively).[20,21]

Pd–O–C and Ni–O–C angles (121.4–124.4°) in the phenol and alcohol adducts **3**, **12**, and **22** are smaller than corresponding Pd–O1–C8 angle (127.1°) in **13**, the palladium phenoxide without phenol, probably due to steric repulsion between the phenoxide ligand and hydrogen-bonded phenol (or 2,2,2-trifluoro-1-phenylethanol).

IR and NMR Spectra of the Alkoxide (Phenoxide) Complexes. IR spectra of hydrogen-bonded complexes **1**–**12** in KBr disks show a broad peak in the range 2350–2700 cm^{-1}. The absorption corresponds to ν(OH) vibration of the hydrogen-bonded OH group in the fluorinated alcohol and phenol.

^{1}H NMR spectra of complexes **1**–**12** show a relatively broad signal due to the OH hydrogen at 12.8–8.9 ppm, and these peak positions are much less shielded than those in the corresponding

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(25) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960. (a) p 265, (b) p 143.

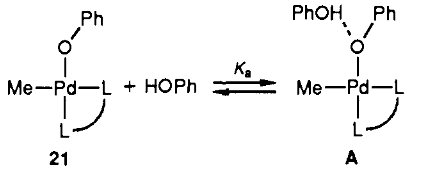
unassociated alcohols (4.53 ppm for $HOCH(CF_3)Ph$) and substituted and nonsubstituted phenols (4.8–5.8 ppm). This indicates the presence of O–H···O hydrogen bonding between the alcohol (or phenol) and the alkoxide (or phenoxide) ligand in solution.[24b,25b,26]

The ^1H NMR spectrum of alcohol-bonded alkoxide complex **1** at –40 °C shows two sets of quartet signals at 5.12 and 4.74 ppm (J_{H-F} = 7.5 Hz). Addition of an equimolar amount of 2,2,2-trifluoro-1-phenylethanol to **1** at –40 °C causes an increase in intensity of the signal at 5.12 ppm with slight broadening. Free 2,2,2-trifluoro-1-phenylethanol shows its OCH hydrogen signal at 4.84 ppm with J_{H-F} = 6.8 Hz. The $^{13}C\{^1H\}$ NMR spectrum of **1** at –60 °C shows signals due to the OCH carbons at 78.3 and 70.7 ppm and signals due to the CF_3 carbons at 126.5 and 125.2 ppm, respectively. The intensity of the latter signal of each pair increased on addition of an equimolar amount of 2,2,2-trifluoro-1-phenylethanol. The change in the $^{13}C\{^1H\}$ NMR spectrum of **1** with added alcohol is in line with the ^1H NMR observation, indicating that the associated alcohol exchanges with free alcohol rapidly. ^1H and $^{13}C\{^1H\}$ NMR spectra of complexes **3–5** also show signals due to aryloxide ligands and associated phenols.

The ^1H NMR spectra of alcohol-bonded methylpalladium phenoxide complexes **22** and **23** show their signals due to OH hydrogens at 10.0 and 11.9 ppm, respectively, indicating the presence of strong O–H···O hydrogen bonding between the fluorinated alcohol and the phenoxide ligand. The $^{13}C\{^1H\}$ NMR spectrum of **22** shows a signal due to the tertiary OCH carbon at 70.9 ppm and signals due to the phenyl carbons at 167.5, 128.1, 118.2, and 113.2 ppm, respectively. The chemical shift (70.9 ppm) of the OCH carbon in **22** is quite similar to that of the associated $HOCH(CF_3)Ph$ (70.7 ppm) in **1** and is different from the chemical shift (78.3 ppm) of the alkoxide ligand in **1**. Peak positions of the phenoxide carbons in **22** resemble those of the phenoxide ligands in **3** and **13** rather than those of the associated phenol in **3**. The $^{13}C\{^1H\}$ NMR spectrum of **23** shows the phenoxide carbons at positions similar to those of the phenoxide ligands in **3** and **13**. These results clearly indicate that **22** and **23** have phenoxide ligands bonded with fluorinated alcohols through O–H···O hydrogen bonding.

Association of Phenol with Methylpalladium Phenoxide Complexes 13, 20, and 21. ^1H NMR spectra of mixtures of the bis(tertiary phosphine)-coordinated phenoxide complexes **20** and **21** with equimolar amounts of phenol show OH hydrogen signals at 12.3 and 12.7 ppm, respectively, at –40 °C in CD_2Cl_2. These peak positions indicate the presence of strong hydrogen bonding between phenol and the phenoxide ligand. Isolation of PdMe(OPh)(HOPh)(dmpe) or PdMe(OPh)(HOPh)(dpe) from the mixtures is not successful probably due to lower solubility of **20** and **21** than the above methylpalladium phenoxide complexes with asssociated phenols.

The chemical shift of the OH hydrogen observed in mixtures of phenol and **21** varies depending on the initial relative concentrations of phenol and **21**. The spectra of mixtures of phenol (fixed at 0.055 M) and **21** (varied from 0.108 to 0.329 M) show the OH resonance in the range 10.5–11.2 ppm, and the peak shifts to lower magnetic field with an increase in the concentration of **21**. Equilibrium constants of association, shown in eq 7 are



(7)

obtained from the relationship between the peak positions and concentration of the compounds in the equilibrated mixture on the basis of the Scatchard equation.[24b] The temperature dependence of the equilibrium constants K_a is shown in Figure 5. Thermodynamic parameters for the association of phenol with **21** derived from the temperature dependence of K_a are $\Delta G°$ = –2.8 kcal mol^{-1}, $\Delta H°$ = –4.1 kcal mol^{-1}, and $\Delta S°$ = –4.0 eu at 300 K. Similarly obtained are thermodynamic parameters for association of phenol with the PMe_3-coordinated phenoxide **13**: $\Delta G°$ = –3.8 kcal mol^{-1}, $\Delta H°$ = –5.6 kcal mol^{-1}, and $\Delta S°$ = –6.0 eu at 300 K. The difference in $\Delta H°$ values in association equilibria of these two complexes with phenol probably arises from the fact that the electron density on the coordinating oxygen in chelate complex **21** is lower than that in *trans*-PMe_3-coordinated complex **13**. The phenoxide ligand at the position trans to the electron-donating methyl ligand may be more electron-rich and act as a stronger proton acceptor than that in **21**.

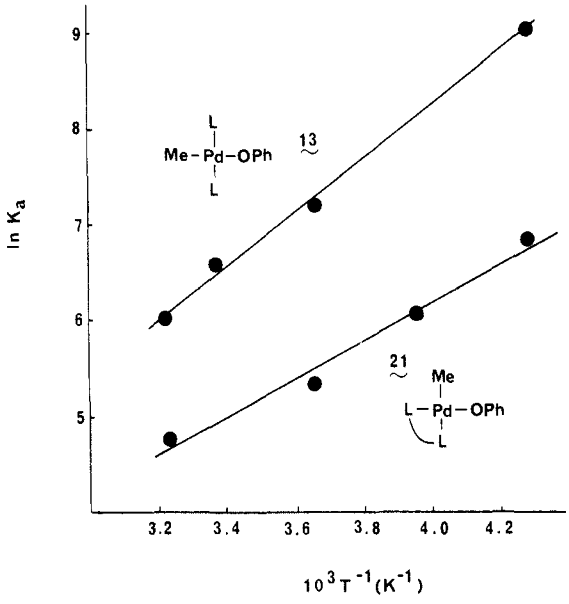
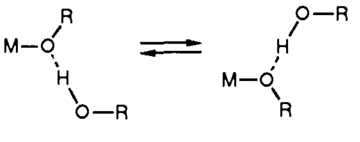


Figure 5. Plot of ln K_a vs T^{-1} for association equilibrium of phenol with *trans*-$PdMe(OPh)(PMe_3)_2$ (**13**) and *cis*-PdMe(OPh)(dmpe) (**21**).

Intramolecular Exchange of Alkoxide Group between Alkoxide Ligand and Hydrogen-Bonded Alcohol. The ^1H NMR spectra of **1** at –60 to –40 °C show pairs of quartet signals due to the OCH hydrogens in the fluoro alkoxide ligand and to the hydrogen-bonded fluoro alcohol at 4.74 and 5.12 ppm, respectively. Raising the temperature of the solution causes broadening of the pair of quartets at low temperatures with coalescence at 273 K. Further warming leads to the appearance of a quartet at 4.93 ppm. Figure 6 shows the change of the OCH hydrogen region in a temperature-dependent ^1H NMR spectrum of **1**. The $^{13}C\{^1H\}$ NMR spectrum of **1** at –60 °C likewise shows two quartets due to the alkoxide ligand and to the hydrogen-bonded alcohol, each coupled to the fluorine nuclei of the CF_3 group. These signals also coalesce when the temperature is raised. Phenol-bonded phenoxide complexes **3**, **8**, and **12** also show similar coalescence of $^{13}C\{^1H\}$ signals arising from the aryloxide ligand and associated substituted or nonsubstituted phenols near room temperature.

The most reasonable mechanism for the observed NMR behavior is the intramolecular exchange (eq 8) of alkoxo group between the alkoxide ligand and the associated alcohol on the NMR time scale, as was shown in the previous report on Rh aryloxide having associated substituted phenol.[20] Change of the



(8)

concentration of the complexes does not influence the rate constant in the exchange reaction, indicating that this reaction proceeds mainly through an intramolecular mechanism. Figure 7 shows relationship between ln *k* and T^{-1} as determined by means of ^1H as well as $^{13}C\{^1H\}$ NMR spectroscopy. Kinetic parameters for the exchange reaction obtained from temperature dependence of *k* are summarized in Table III.

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[26] Murthy, A. S. N.; Rao, C. N. R. *Appl. Spectrosc. Rev.* **1968**, *2*, 69.

Table III. Kinetic Data of Intramolecular Exchange of Alkoxide or Aryloxide Groups of the Complexes[a,b]

complex	k (s^{-1}) at temp (K) 213	233	253	263	268	273	278	283	293	297	308	T_c (K) ^1H	$^{13}C\{^1H\}$	$\Delta G_{300}^{\ddagger}$ (kcal mol^{-1})
1		13.6	109		431					2580		268[c]		12.7
3		8.5	10.6			63.3		81.1		134	170		278	14.6
4		0.7	6.8			34.8	52.7		80.0			283		14.5
5		0.7	6.0	14.3		40.3		56.9		101[d]		278		14.5
8	47.0	61.3	67.9			81.6	99.2						283	14.8

[a] Rate constants k and coalescence temperatures T_c are obtained from ^1H NMR at 500 MHz or $^{13}C\{^1H\}$ NMR at 125 MHz in CD_2Cl_2. [b] Rate constants and coalescence temperatures were determined by observation of resonances for complexes **1–8** arising from ortho hydrogens of the phenoxide group (for k of **1**), meta carbons of the phenoxide group (**3** and **8**), methyl hydrogens of *p*-methylphenoxide group (**4**), and methyl hydrogens of the *p*-methoxyphenoxide group (**5**). [c] Obtained from signals due to OCH hydrogens of the fluoro alkoxide group. [d] Data at 295.5 K.

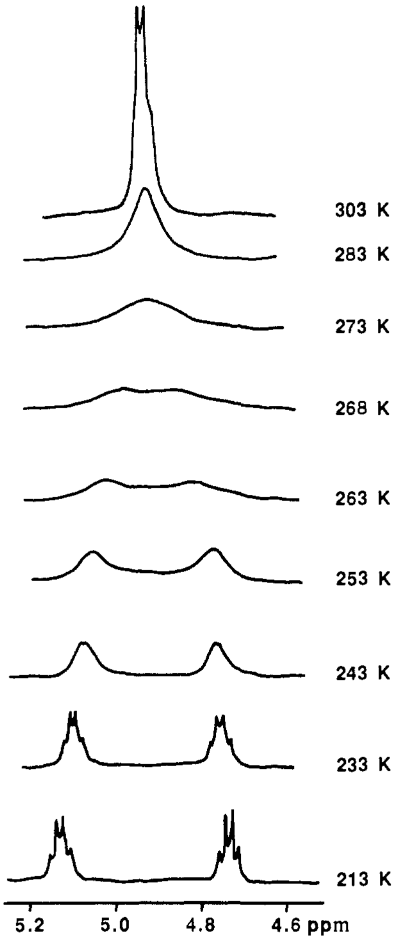


Figure 6. Change of the resonances with temperature of the OCH hydrogens in *trans*-$PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$ (**1**) in CD_2Cl_2 observed at 500 MHz.

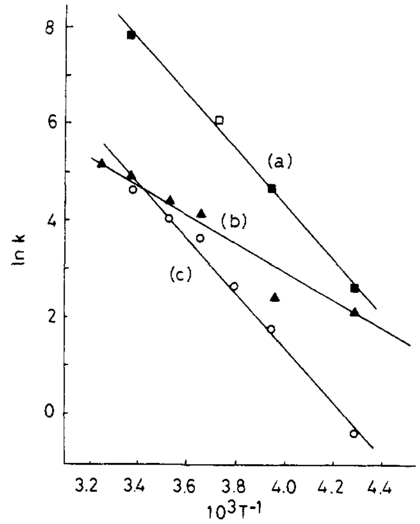
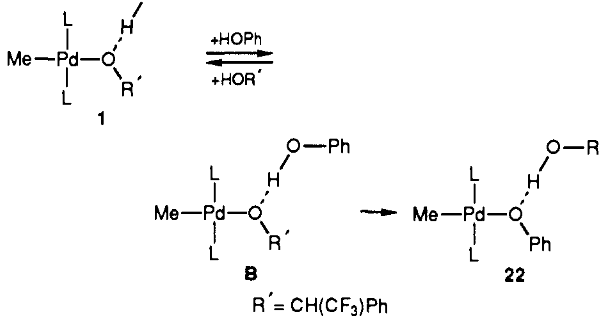


Figure 7. Arrhenius plots of intramolecular exchange of an alkoxide (or aryloxide) group between alkoxide (or aryloxide) ligand and hydrogen-bonded alcohol (or substituted and nonsubstituted phenol): (a) $PdMe(OCH(CF_3)Ph)(HOCH(CF_3)Ph)(PMe_3)_2$ (**1**); (b) $PdMe(OPh)(HOPh)(PMe_3)_2$ (**3**); (c) $PdMe(OC_6H_4\text{-}p\text{-}OMe)(HOC_6H_4\text{-}p\text{-}OMe)(PMe_3)_2$ (**5**). ○ and □ are determined by ^1H NMR spectra and ▲ and ■ are determined by $^{13}C\{^1H\}$ NMR spectra in CD_2Cl_2.

Displacement of Alkoxide Ligand in 1 with Phenoxide Group by Addition of Phenol. We have further studied exchange reactions of externally added phenol with the alkoxide ligand in methylpalladium alkoxide complex **1**. The exchange reaction (eq 9) proceeded smoothly to give alcohol-bonded phenoxide complex **22** that was obtained independently (eq 6) by bonding of the alcohol with nonassociated methylpalladium phenoxide **13**. The identity of **22** was established by comparison of its IR and ^1H NMR spectra with those of **22** prepared by eq 6.



(9)

A probable pathway from **1** to **22** is initial exchange of the associated alcohol in **1** with added phenol to give a phenol-bonded complex **B** that gives **22** by an intramolecular exchange process. Examination of the $^{13}C\{^1H\}$ NMR spectrum of an equimolar mixture of phenol and **1** at −60 °C showed absence of any intermediate and complete conversion of **1** into **22**. The alcohol-bonded phenoxide complex **22** seems to be much more stable than the assumed intermediate **B** having the phenol-bonded alkoxide ligand.

Reaction of 2 equiv of phenol with alcohol-bonded alkoxide **1** gives the phenol-bonded phenoxide complex **3** in quantitative yield. The reaction probably proceeds through **22** to **3** by exchange of the associated alcohol in **22** with phenol as shown below.

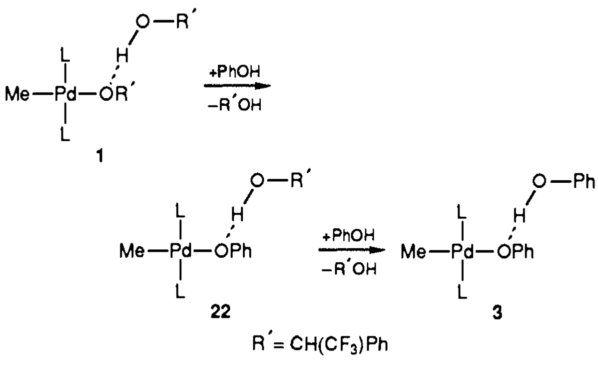


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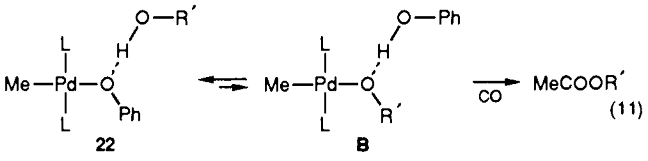
Table IV. Reactions of the Methylpalladium Alkoxide and Phenoxide Complexes with CO[a]

complex	conditions: solvent	conditions: time (h)	product (% yield)[b]
1	Et_2O	2	$MeCOO(CH(CF_3)Ph)$ (99)
3	CH_2Cl_2	3	MeCOOPh (31)
13	CH_2Cl_2	3	MeCOOPh (16)
20	toluene	2	MeCOOPh (trace)[c]
22	Et_2O	1.5	$MeCOOCH(CF_3)Ph$ (46) HOPh (54)

[a] Reactions were carried out under 1 atm of CO at room temperature. [b] Yields based on Pd, determined by GC. [c] NMR analysis of the product indicated the presence of 70% of unreacted **20**.

Reaction of CO with Alkylmetal Alkoxide or Phenoxide Complexes. We have previously observed that carboxylic esters undergo C–O bond cleavage when they oxidatively add to nickel(0) and palladium(0) complexes.[27] Furthermore, we observed the reverse process, C–O bond formation, when carboxylic esters are formed from alkylnickel and -palladium aryloxide complexes and carbon monoxide.[23] In the latter case, CO inserted into the alkyl–nickel and –palladium bonds to afford acylmetal aryloxides and the acyl aryloxide groups then underwent reductive elimination. On the other hand, in the reaction of $PdMe(OCH(CF_3)_2)(dpe)$ with CO to give $MeCOOCH(CF_3)_2$, evidence was provided to show that CO inserted into the Pd–alkoxide bond to give $PdMe(COOCH(CF_3)_2)(dpe)$, which released the acetate on reductive elimination.[22a] The dichotomy in the behavior of methylpalladium aryloxide and methylpalladium alkoxide toward CO is intriguing. Thus, we have examined reactivities of the isolated methylpalladium alkoxides and phenoxides toward carbon monoxide to compare their abilities to produce acetate esters.

Table IV summarizes results of the reactions of CO (1 atm) with the alcohol-bonded alkoxides, with phenoxides with and without phenol, and with the alcohol-bonded phenoxide complexes **1**, **3**, **13**, **20**, and **22** at room temperature. Reaction of CO with alcohol-bonded alkoxide complex **1** gave a quantitative yield of the corresponding ester $MeCOOCH(CF_3)Ph$, while reaction of CO with the phenoxide complexes **3** and **13** gave much smaller amounts of phenyl acetate under similar reaction conditions. The former reaction probably involves insertion of CO into the Pd–alkoxide bond to give a methylpalladium complex having the alkoxycarbonyl ligand that reductively eliminates the ester; this behavior is similar to that assumed to occur in the carbonylation of $PdMe(OCH(CF_3)_2)(dpe)$. The low yields of phenyl acetate in the reaction of CO with phenol-bonded and phenol-free methylpalladium phenoxides **3** and **13** are in agreement with our previous observation of the low reactivity of the methylpalladium phenoxide complexes toward CO to give acetylpalladium aryloxide complexes. The dpe-coordinated methylpalladium phenoxide complex showed even lower reactivity. The lower reactivity of methylpalladium phenoxides **3**, **13**, and **20** toward CO may be due to their reluctance to undergo the CO insertion into the Me–Pd bond rather into the Pd–OPh bond. In this context, the reaction of CO with alcohol-bonded methylpalladium phenoxide is intriguing. The reaction gave no phenyl acetate but released only $CH_3COOCH(CF_3)Ph$ with liberation of phenol. Formation of these products suggests CO insertion into the Pd–$OCH(CF_3)Ph$ bond in complex **B**, which may be formed by the following reaction course:



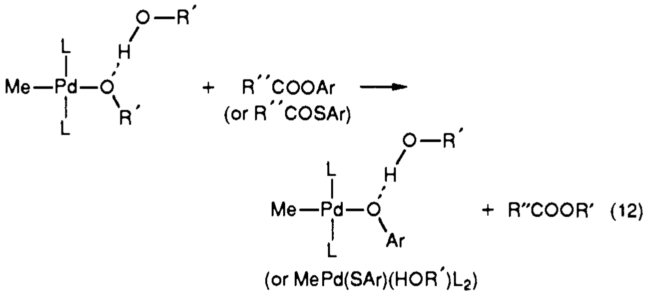
22 **B**

R' = $CH(CF_3)Ph$

We could not spectroscopically detect complex **B** by examination of ^{13}C NMR of **22** at −60 °C, and the above preequilibrium between **22** and **B** seems to be favorable for formation of starting complex **22**. However, formation of $CH_3COOCH(CF_3)Ph$ through **B** should still be possible if reactivity of alkoxide complex **B** toward CO is high as shown in the reaction of **1** with CO.

Reactions of Methylpalladium Alkoxide Complexes with Carboxylic and Carbothioic Esters. Reactions of alcohol-bonded alkylpalladium alkoxide complex **1** with equimolar amounts of phenyl acetate and propionate proceed smoothly at room temperature to give alcohol-bonded phenoxide complex **22** together with 2,2,2-trifluoro-1-phenylethyl acetate and propionate in 85% and 70% yields, respectively. Complex **1** reacts also with several other carboxylic and carbothioic esters such as $MeCOOC_6H_4$-*p*-CN and MeCOSPh to give 2,2,2-trifluoro-1-phenylethyl acetate and nonassociated palladium complexes with aryloxide and aryl thiolate ligands. Table V summarizes the results of these reactions.

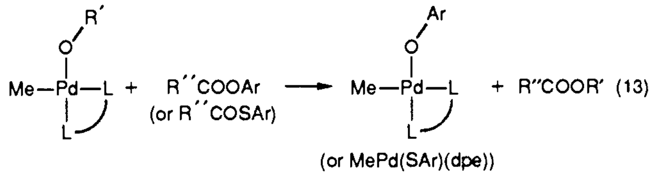
The results of the transesterification indicate that the aryloxide or aryl thiolate entity in the esters is exchanged with the alkoxide ligand in complex **1** and $PdMe(OCH(CF_3)Ph)(dpe)$ to give methylpalladium aryloxide (or aryl thiolate) with liberation of the alkoxide ligand as the fluoroalkyl esters (eq 12).



L = PMe_3; R' = $CH(CF_3)Ph$; R'' = Me, Et, Ph

As we have observed previously, phenols are exchanged preferentially with the fluoro alkoxide ligand in **21** to give the phenoxides liberating the fluoro alcohols. It is interesting that the aryloxide (or aryl thiolate) entity in the esters is exchanged readily with the alkoxide ligand in **1**. The driving factor for both types of exchange reactions may be the fact that the aryloxide ligand is more stable than the alkoxide ligand.

As the reactions of $PdMe(OCH(CF_3)Ph)(dpe)$ with aryl esters show, the exchange reactions are not limited to the alcohol-bonded alkoxide complexes. The aryloxide entities in aryl esters were found to be readily exchanged with the alkoxide ligand in the alcohol-free alkoxide complex.



L‿L = dpe; R' = $CH(CF_3)Ph$; R'' = Me, Ph

The results of the exchange reactions obtained in the present study indicated operation of the following two exchange processes.

$$\text{M-OR}' + \text{MeC(O)OPh} \rightarrow \text{M-OPh} + \text{MeC(O)OR}' \quad \text{(i)}$$

$$\text{M-OPh} + \text{HOR}' \rightleftarrows \text{M-OR}' + \text{H-OPh} \quad \text{(ii)}$$

$$\text{M} = \text{PdMe(dpe)}$$

The ready occurrence of the stoichiometric transesterification between the palladium alkoxides and aryl esters (eq i) and of further exchange processes (ii) between the phenoxide and alcohol prompted us to examine the feasibility of catalytic transesterification promoted by a palladium alkoxide complex.

Indeed the transesterification reaction between phenyl acetate (10 equiv/Pd) and 2,2,2-trifluoro-1-phenylethanol (200 equiv/Pd)

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(27) (a) Yamamoto, T.; Ishizu, J.; Kohara, T.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 3758. (b) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 6863. (c) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559.

Table V. Reactions of Methylpalladium Alkoxide Complexes with Aryl Esters

reaction[a]			product	
complex[b]	ester	time (h)	complex[c] (% yield)	ester[d] (% yield)
A	MeCOOPh	12	**22** (85)	$MeCOOCH(CF_3)Ph$ (70)
A	EtCOOPh	13	**22** (73)	$EtCOOCH(CF_3)Ph$ (91)
A	$MeCOOC_6H_4$-*p*-CN	2	$PdMe(OC_6H_4$-*p*-$CN)(PMe_3)_2$ (76)	$MeCOOCH(CF_3)Ph$ (79)
A	MeCOSPh	12	$PdMe(SPh)(PMe_3)_2$[e] (76)	$MeCOOCH(CF_3)Ph$ (80)
B	MeCOOPh	12	PdMe(OPh)(dpe) (84)	$MeCOOCH(CF_3)Ph$ (57)
B	$MeCOOC_6H_4$-*p*-CN	4	$PdMe(OC_6H_4$-*p*-CN)(dpe)[e] (83)	$MeCOOCH(CF_3)Ph$ (79)
B	EtCOOPh	8	PdMe(OPh)(dpe) (70)	$EtCOOCH(CF_3)Ph$ (68)
B	MeCOSPh	2	PdMe(SPh)(dpe) (74)	$MeCOOCH(CF_3)Ph$ (85)
B	PhCOSPh	2	PdMe(SPh)(dpe) (75)	$PhCOOCH(CF_3)Ph$ (82)
B	PhCOOPh	2.5	PdMe(OPh)(dpe) (88)	$PhCOOCH(CF_3)Ph$ (97)

[a] Reaction was carried out by stirring a mixture of a palladium complex (0.033 mmol) and equimolar ester in Et_2O or THF at room temperature. [b] **A**, **1**; **B**, $PdMe(OCH(CF_3)Ph)(dpe)$. [c] Isolated yields are shown in parentheses. [d] GLC yields are shown in parentheses. [e] See the Experimental Section for characterization of these new complexes. The other complexes are characterized by comparison of their NMR spectra with the reported data.

catalyzed by $PdMe(OCH(CF_3)Ph)(dpe)$ proceeded at room temperature to give $MeCOOCH(CF_3)Ph$ (4.6 equiv/Pd) (see the Experimental Section).

$$MeCOOPh + HOCH(CF_3)Ph \xrightarrow{Pd} MeCOOCH(CF_3)Ph + PhOH \quad (14)$$

Although alkoxides of various metals such as aluminum, zinc, and titanium are often used as catalysts for transesterification, the mechanistic details have so far remained unclarified. The results obtained here provide useful information regarding important steps in transesterification catalyzed by metal alkoxides. Particularly relevant is the behavior of the alcohol-bonded metal alkoxide that may be regarded as a key species in the alcohol-exchange reactions. The structures of the hydrogen-bonded alcohol adducts of the palladium alkoxides, which undergo rapid intramolecular and intermolecular exchange reactions, suggest a possible mode of interaction in the catalytic transesterification reactions.

Concluding Remarks

The present study revealed that dialkylnickel and -palladium complexes readily form stable alkoxide complexes on treatment with fluorinated alcohols and phenols. The alkoxides are stable to β-hydrogen elimination. The oxygen atoms in the alkoxides and phenoxides are electron-rich, particularly when they are situated trans to the alkyl ligand and form strong hydrogen bonds with the acidic alcohols or phenols. X-ray diffraction and NMR studies revealed detailed structural features of the O–H···O hydrogen bonding between the alkoxide (aryloxide) and the alcohol (phenol) in the solid state as well as in solution.

The hydrogen-bonded alcohol readily exchanges with the alkoxide ligand in the alkoxide complexes through an intramolecular process. Added alcohol or phenol rapidly exchanges with the hydrogen-bonded alcohol and further with the alkoxide ligand.

Furthermore, exchange of the alkoxide ligand with the aryloxide group in aryl carboxylate was confirmed. Thus, a series of probable elementary steps in transesterification promoted by a metal alkoxide was established. On the basis of above findings, a catalytic transesterification process promoted by a palladium complex was developed.

The present study revealed that fluoro alkoxide is more labile than phenoxide in the exchange reactions. The lability of the alkoxide ligand is also in line with preferential formation of fluoroacetate in the reaction of the alcohol-bonded palladium phenoxide with CO. Assumption of facile CO insertion into the Pd–alkoxide ligand in methylpalladium alkoxide to give methylpalladium alkoxycarbonyl complex reasonably accounts for the formation of fluoroalkyl acetate liberated by subsequent reductive elimination.

The basic knowledge provided in the present study may be useful in helping elucidate reaction mechanisms of some metal-promoted organic reactions as well as in development of new synthetic organic reactions.

Experimental Section

All manipulations of the complexes were performed under N_2 or argon by using Schlenk flasks. 1,1,1,3,3,3-Hexafluoro-2-propanol was purchased from Tokyo Kasei Co. Ltd. Dmpe was purchased from Strem Chemicals Co. 2,2,2-Trifluoro-1-phenylethanol was prepared by $LiAlH_4$ reduction of 2,2,2-trifluoroacetophenone. PMe_3 was prepared from MeMgI and $P(OPh)_3$ and used as an Et_2O solution after repeated distillation. $PdMe_2(dpe)$ and *cis*-$PdMe_2(PMePh_2)_2$ were prepared according to the literature.[28a,b]

Elemental analyses were carried out by Dr. M. Tanaka and T. Saito of our laboratory by using a Yanagimoto CHN autocorder, Type MT-2, and Yazawa halogen analyzer. NMR (^1H, ^{19}F, ^{31}P, ^{13}C) spectra were recorded on JEOL FX-100 and GX-500 spectrometers by Dr. Y. Nakamura, R. Ito, and A. Kajiwara of our laboratory. IR spectra were recorded on a Jasco IR-810 spectrophotometer.

Crystal Structure Determination and Refinement. Intensity data for **3**, **12**, **13**, and **22** were collected at 20 °C on a Rigaku AFC-5 diffractometer. Accurate cell dimensions were obtained from the setting angles of 25 reflections. Three reflections, monitored after every 100 reflections, showed no significant intensity degradation during the data collection except for those of **12**, whose intensities decreased up to 93%. No absorption correction was applied.

Each structure was solved by common Fourier methods. Details of the refinement determination are given in Table I. A full-matrix least-squares procedure was applied to refine the structures with anisotropic temperature factors for all the non-hydrogen atoms. Hydrogen atoms that were extracted from difference Fourier map were included in the least-squares calculations, but their parameters were not refined.

Calculations were carried out with the programs SAPI85 and ORTEP on a FACOM A-70.

Preparation of *trans*-$PdMe_2(PMe_3)_2$. $AlMe_2(OEt)$ (3.8 mL, 29 mmol) was added dropwise to a mixture of $Pd(acac)_2$ (1.5 g, 5.0 mmol) and PMe_3 (0.91 g, 12 mmol) in Et_2O (35 mL) at −60 °C. Raising the temperature to −20 °C and stirring the reaction mixture for 2 h gave a white solid, which was filtered, washed with hexane, and dried in vacuo. Recrystallization from Et_2O gave colorless crystals of *trans*-$PdMe_2(PMe_3)_2$: 0.62 g, 43%; ^1H NMR (CD_2Cl_2 at −20 °C, ppm) −0.64 (t, Pd–CH_3, J(H–P) = 18 Hz), 1.28 (app t due to virtual coupling, P–CH_3, J(H–P) = 3.1 Hz). Anal. Calcd for $C_8H_{24}P_2Pd$: C, 33.3; H, 8.4. Found: C, 33.1; H, 8.2.

trans-$PdEt_2(PMe_3)_2$ was prepared similarly by the reaction of $Pd(acac)_2$, $Al_2Et_3(OEt)_3$, and PMe_3 in ether by a procedure used in our group.[28c]

Preparation of $PdMe_2$(dmpe). The complex was prepared by a modified literature method.[29]

Dmpe (0.61 g, 3.3 mmol) was added dropwise to *cis*-$PdMe_2(PMePh_2)_2$ (1.7 g, 3.2 mmol) dispersed in Et_2O (60 mL) at room temperature. The reaction mixture gradually turned into a colorless solution. After the mixture was stirred for 2 h, the solvent was removed under reduced pressure to give $PdMe_2$(dmpe) as a white solid, which was recrystallized from ether; 0.73 g, 80%.

Preparation of *trans*-$NiMe_2(PMe_3)_2$. The complex was prepared by a modified literature method.[30]

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(28) (a) Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319. (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (c) Son, T.-I.; Ozawa, F.; Yamamoto, A. Unpublished results.

(29) Tooze, R.; Chiu, K. W.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1025.

(30) Klein, H. F.; Karsh, H. H. *Chem. Ber.* **1972**, *105*, 2628.

AlMe$_2$(OEt) (6.5 mL, 50 mmol) was added to a mixture of Ni(acac)$_2$ (3.0 g, 12 mmol) and PMe$_3$ (1.8 g, 24 mmol) in Et$_2$O at -70 °C. Color of the reaction mixture turned immediately from purple to dark yellow. Raising the temperature to -30 °C followed by 2-h stirring at the temperature gave a red solution. Reducing the volume of the solvent to ca. 20 mL followed by cooling to -70 °C gave orange crystals of *trans*-NiMe$_2$(PMe$_3$)$_2$: 0.93 g, 33%; ^{1}H NMR (CD$_2$Cl$_2$ at -40 °C, ppm) -1.21 (t, NiC*H*$_3$, *J*(H-P) = 9.5 Hz), 1.13 (br s, PC*H*$_3$).

Preparation of 1 and 2. 2,2,2-Trifluoro-1-phenylethanol (390 mg, 2.2 mmol) was added to an Et$_2$O (7 mL) solution of *trans*-PdMe$_2$(PMe$_3$)$_2$ (320 mg, 1.1 mmol) at -30 °C. Raising the temperature to 0 °C and stirring the reaction mixture for 2 h gave a colorless solution. Evaporation of the solvent left a white solid of **1** that was recrystallized from Et$_2$O: 400 mg, 57%; ^{1}H NMR (500 MHz in CD$_2$Cl$_2$ at -40 °C, ppm) -0.16 (Pd–C*H*$_3$, t, *J*(PH) = 7.0 Hz), 1.07 (P(C*H*$_3$)$_3$, app t by virtual coupling, observed splitting 3.1 Hz), 4.74 and 5.12 (OC*H* of the alkoxide ligand and the associated alcohol, respectively, q, *J*(F–H) = 7.5 Hz), 10.0 (O*H*, s); ^{13}C NMR (68 MHz in CD$_2$Cl$_2$ at -40 °C, ppm) -11.40 (Pd–*C*H$_3$, t, *J*(P–C) = 7.4 Hz), 12.11 (P(*C*H$_3$)$_3$, app t by virtual coupling, observed splitting 13.4 Hz), 78.27 and 70.66 (O*C*H of the alkoxide ligand and the associated alcohol, respectively, q, *J*(F–C) = 6.1 Hz), 126.5 and 125.2 (*C*F$_3$ of the alkoxide ligand and the associated alcohol, respectively, q, *J*(F–C) = 288 and 283 Hz, respectively).

Complex **2** was prepared analogously.

Preparation of 3–10. Phenol (210 mg, 2.2 mmol) was added to an Et$_2$O (8 mL) solution of *trans*-PdMe$_2$(PMe$_3$)$_2$ (310 mg, 1.1 mmol) at -25 °C. Stirring the reaction mixture for 1 h below 0 °C caused precipitation of a white solid of **3**, which was filtered, washed with Et$_2$O, and recrystallized from CH$_2$Cl$_2$–hexane (3:2): 200 mg, 41%; ^{1}H NMR (100 MHz in CD$_2$Cl$_2$ at -40 °C, ppm) 0.14 (Pd–C*H*$_3$, t, *J*(PH) = 7.0 Hz), 1.23 (P(C*H*$_3$)$_3$, app t by virtual coupling, observed splitting 3.2 Hz), 12.8 (O*H*, s); ^{13}C NMR (125 MHz in CD$_2$Cl$_2$ at -40 °C, ppm) -11.55 (Pd–*C*H$_3$, t, *J*(P–C) = 6.5 Hz), 12.40 (P(*C*H$_3$)$_3$, app t by virtual coupling, observed splitting 14.2 Hz), 113.5, 118.3, 129.2, and 167.1 (para, ortho, meta, and ipso carbons of the phenoxide ligand), 115.7, 114.8, 128.9, and 158.6 (ortho, para, meta, and ipso carbons of the associated phenol).

Complexes **4–10** were prepared analogously.

Preparation of 11 and 12. Phenol (100 mg, 1.1 mmol) was added dropwise to *trans*-NiMe$_2$(PMe$_3$)$_2$ (130 mg, 0.54 mmol) dispersed in Et$_2$O (8 mL) at -40 °C. Raising the temperature to 0 °C gave a yellow solution, from which a yellow solid deposited on stirring. The solid was filtered, washed with pentane, and recrystallized from Et$_2$O to give yellow crystals of **12**, 210 mg, 94%.

Complex **11** was prepared analogously.

Preparation of 13–19. Phenol (94 mg, 1.0 mmol) was added slowly to an Et$_2$O (7 mL) solution of *trans*-PdMe$_2$(PMe$_3$)$_2$ (290 mg, 1.0 mmol) at room temperature. Stirring the reaction mixture for 3 h caused precipitation of a white solid of **13**, which was filtered, washed with hexane and Et$_2$O, and dried in vacuo: 230 mg, 61%; ^{1}H NMR (100 MHz in CD$_2$Cl$_2$ at -40 °C, ppm) 0.08 (Pd–C*H*$_3$, t, *J*(PH) = 7.0 Hz), 1.16 (P(C*H*$_3$)$_3$, app t by virtual coupling, observed splitting 3.3 Hz); ^{13}C NMR (68 MHz in CD$_2$Cl$_2$ at -40 °C) -13.27 (Pd–*C*H$_3$, t, *J*(P–C) = 5.9 Hz), 13.14 (P(*C*H$_3$)$_3$, app t by virtual coupling, observed splitting 13.7 Hz), 111.5, 119.5, 129.9, and 171.4 (para, ortho, meta, and ipso carbons of the phenoxide ligand).

Complexes **14–19** were prepared analogously.

Preparation of 20 and 21. Phenol (45 mg, 0.48 mmol) was added to PdMe$_2$(dpe) (260 mg, 0.48 mmol) dispersed in toluene (4 mL) at room temperature. After the solution was stirred for 30 min, hexane was added to cause precipitation of **20**, which was filtered and recrystallized from CH$_2$Cl$_2$–hexane (1:1); 360 mg, 75%.

Complex **21** was prepared analogously (92%).

Preparation of 22 and 23. 1,1,1-Trifluoro-2-phenylethanol (110 mg, 0.64 mmol) was added to *trans*-PdMe(OPh)(PMe$_3$)$_2$ (200 mg, 0.55 mmol) in Et$_2$O (8 mL) at room temperature. The reaction mixture soon turned into a homogeneous solution. After the solution was stirred for 1 h, the solvent was removed under reduced pressure to give **22** as a white solid, which was filtered and recrystallized from ether containing a small amount of 2,2,2-trifluoro-1-phenylethanol: 220 mg, 75%; ^{1}H NMR (100 MHz in CD$_2$Cl$_2$ at -40 °C, ppm) 0.04 (Pd–C*H*$_3$, t, *J*(PH) = 7.0 Hz), 1.11 (P(C*H*$_3$)$_3$, app t by virtual coupling, observed splitting 3.3 Hz), 10.0 (O*H*, s); ^{13}C NMR (125 MHz in CD$_2$Cl$_2$ at -40 °C, ppm) -11.93 (Pd–*C*H$_3$, t, *J*(P–C) = 6.7 Hz), 12.14 (P(*C*H$_3$)$_3$, app t by virtual coupling, observed splitting 14.3 Hz), 113.2, 118.2, 128.1, and 167.5 (para, ortho, meta, and ipso carbons of the phenoxide ligand), 70.9 (OCH, q, *J*(F–H) = 29.8 Hz), 125.1 (CF$_3$, q, *J*(F–H) = 283 Hz).

Complex **23** was prepared analogously (81%).

Estimation of the Associated Constants. Six NMR samples containing phenol at a fixed concentration (0.055 M) and **21** at various concentrations (0.108–0.329 M) in CD$_2$Cl$_2$ were prepared. ^{1}H NMR spectra of the samples were measured at several fixed temperatures. Chemical shifts of the OH hydrogens, $\delta(\mathrm{OH})_{\mathrm{obs}}$, are obtained at each temperature. K_a value is determined by calculation on the basis of the following equation (Scatchard equation[24b])

$$\frac{\delta(\mathrm{OH})_{\mathrm{obs}} - \delta(\mathrm{OH})_{\mathrm{PhOH}}}{[\mathbf{21}]_{\mathrm{eq}}} = -K_a(\delta(\mathrm{OH})_{\mathrm{obs}} - \delta(\mathrm{OH})_{\mathrm{PhOH}}) + Z$$

where $\delta(\mathrm{OH})_{\mathrm{obs}}$ = chemical shift of the observed OH signal in the equilibrium mixture, $\delta(\mathrm{OH})_{\mathrm{PhOH}}$ = chemical shift of free PhOH, $[\mathbf{21}]_{\mathrm{eq}}$ = concentration of **21** in the equilibrium mixture, and Z = constant.

Reaction of Phenol with 1. Phenol (32 mg, 0.34 mmol) was added slowly to an Et$_2$O (6 mL) solution of **1** (200 mg, 0.32 mmol). Stirring the reaction mixture for 3 h at 0 °C caused precipitation of a white solid of **22**, which was filtered, washed with hexane and Et$_2$o, and dried in vacuo (150 mg, 83%).

Reaction of CO with 1, 3, and 22. Complex **1** (160 mg, 0.25 mmol) was dissolved in ether (5 mL) at room temperature. After evacuation of the system, CO (1 atm) was introduced at the temperature. The colorless reaction mixture slowly turned to dark red. After the solution was stirred for 2 h, GLC analysis showed the formation of 2,2,2-trifluoro-1-phenylethyl acetate (53 mg, 98%) and 2,2,2-trifluoro-1-phenylethanol (44 mg, 100%). Removal of the solvent gave Pd(CO)$_m$(PMe$_3$)$_n$ as revealed by IR spectroscopy.

Reactions of **3** and **22** with CO were carried out analogously.

Reaction of Methylpalladium Alkoxide Complexes with Esters. Phenyl benzoate (44 mg, 0.33 mmol) was added to an Et$_2$O (6 mL) solution of **1** (204 mg, 0.33 mmol). The initial colorless solution turned to pale yellow on stirring. After the solution was stirred for 12 h, GLC analysis of the reaction mixture showed the formation of 2,2,2-trifluoro-1-phenylethyl acetate, 50 mg, 70%. The solvent was removed under reduced pressure to give a white solid of **22**, which was washed with hexane several times and dried in vacuo; 150 mg, 85%.

Reactions of **1** with other carboxylic and carbothioic esters and reactions of PdMe(OCH(CF$_3$)Ph)(dpe) with esters were carried out analogously. New complexes obtained by these reactions, *trans*-PdMe(SPh)(PMe$_3$)$_2$ and PdMe(OC$_6$H$_4$-p-CN)(dpe), were characterized by NMR spectroscopy and elemental analysis.

***trans*-PdMe(SPh)(PMe$_3$)$_2$**: ^{1}H NMR (CD$_2$Cl$_2$, ppm) 0.16 (Pd–C*H*$_3$, t, 3 H, *J*(P–H) = 6.7 Hz), 1.32 (P–C*H*$_3$, app t due to virtual coupling). Anal. Calcd for C$_{13}$H$_{26}$P$_2$SPd: C, 40.8; H, 6.9; S, 8.4. Found: C, 41.2; H, 7.1; S, 8.1.

PdMe(OC$_6$H$_4$-*p*-CN)(dpe): ^{1}H NMR (CD$_2$Cl$_2$, ppm) 1.04 (Pd–C*H*$_3$, q, 3 H, *J*(P–H) = 6.6 and 8.8 Hz).

Transesterification of Phenyl Esters Catalyzed by Palladium Complex. A toluene (3 mL) solution of a mixture of PdMe(OCH(CF$_3$)Ph)(dpe) (60 mg, 0.085 mmol), phenyl acetate (116 mg, 0.85 mmol), and 2,2,2-trifluoro-1-phenylethanol (300 mg, 17 mmol) was stirred for 6 h at room temperature. GLC analysis of the reaction mixture showed formation of MeCOOCH(CF$_3$)Ph (0.36 mmol, 4.2 equiv/Pd).

Extension of the reaction time to 12 h in the reaction of phenyl acetate (4.25 mmol) with the same alcohol (17 mmol) caused an increase in the yield of the fluoroalkyl acetate to 12.6 equiv/Pd.

Similar reactions of phenyl benzoate (198 mg, 0.85 mmol) with 2,2,2-trifluoro-1-phenylethanol (300 mg, 0.17 mmol) for 12 h at room temperature gave PhCOOCH(CF$_3$)Ph (0.47 mmol, 5.6 equiv/Pd).

The palladium complex PdMe(OCH(CF$_3$)Ph)(dpe) did not catalyze transesterification of 2-butyl acetate with 2-methyl-1-propanol.

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Supplementary Material Available: Figures S1–S4, molecular structures of complexes, Tables S1–S12, complete tables of crystallographic results, Tables S17 and S18, tables of yield, melting point, and analytical and NMR (^{1}H, ^{13}C, ^{19}F, and ^{31}P) data of complexes **1–23**, Table S19, equilibrium constants K_a for association of phenol with **13** and **21**, and the detailed calculation procedure (31 pages); Tables S13–S16, observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.