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Insertion Reactions into Pd–O and Pd–N Bonds: Preparation of Alkoxycarbonyl, Carbonato, Carbamato, Thiocarbamate, and Thioureide Complexes of Palladium(II)

José Ruiz,* M. Teresa Martínez, Félix Florenciano, Venancio Rodríguez, and Gregorio López*

Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, 30071 Murcia, Spain

José Pérez

Departamento de Ingeniería Minera, Geológica y Cartográfica (Area de Química Inorgánica), Universidad Politécnica de Cartagena, 30203 Cartagena, Spain

Penny A. Chaloner and Peter B. Hitchcock

School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

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Mononuclear palladium hydroxo complexes of the type [Pd(N–N)(C_6F_5)(OH)] [(N–N = 2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (Me_2bipy), 1,10-phenanthroline (phen), or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda)] have been prepared by reaction of [Pd(N–N)(C_6F_5)(acetone)]ClO_4 with KOH in methanol. These hydroxo complexes react, in methanol, with CO (1 atm, room temperature) to yield the corresponding methoxycarbonyl complexes [Pd(N–N)(C_6F_5)(CO_2Me)]. Similar alkoxycarbonyl complexes [Pd(N–N)(C_6F_5)(CO_2R)] (N–N = bis(3,5-dimethylpyrazol-1-yl)methane); R = Me, Et, or ^{i}Pr) are obtained when [Pd(N–N)(C_6F_5)Cl] is treated with KOH in the corresponding alcohol ROH and CO is bubbled through the solution. The reactions of [Pd(N–N)(C_6F_5)(OH)] (N–N = bipy or Me_2bipy) with CO_2, in tetrahydrofuran, lead to the formation of the binuclear carbonate complexes [(N–N)(C_6F_5)Pd(μ-η^2-CO_3)Pd(C_6F_5)(N–N)]. Complexes [Pd(N–N)(C_6F_5)(OH)] react in alcohol with PhNCS to yield the corresponding *N*-phenyl-*O*-alkylthiocarbamate complexes [Pd(N–N)(C_6F_5){SC(OR)NPh}]. Similarly, the reaction of [Pd(bipy)(C_6F_5)(OH)] with PhNCO in methanol gives the *N*-phenyl-*O*-methylcarbamate complex [Pd(bipy)(C_6F_5){NPhC(O)OR}]. The reactions of [(N–N)Pd(C_6F_5)(OH)] with PhNCS in the presence of Et_2NH yield the corresponding thioureidometal complexes [Pd(N–N)(C_6F_5){NPhCSNR_2}]. The crystal structures of [Pd(tmeda)(C_6F_5)(CO_2Me)], [Pd_2(Me_2bipy)$_2$(C_6F_5)$_2$(μ-η^2-CO_3)]·2CH_2Cl_2, and [Pd(tmeda)(C_6F_5){SC(OMe)NPh}] have been determined.

Introduction

Dimeric hydroxo complexes [M_2R_4(μ-OH)$_2$]$^{2-}$ of the group 10 elements[1] have been shown to be excellent precursors in organic and organometallic synthesis of new compounds.[1f,g,2] The acid−base reaction of these hydroxo complexes with a protic electrophile [M(μ-OH)$_2$M + H(L−L) → M(L−L) or M(μ-L−L)$_2$M + 2H_2O] leads to the formation of mono- or binuclear complexes depending on the *endo*- or *exo*-bidentate nature of the deprotonated (L−L)$^-$ ligand. Aryloxo,[3] amido,[4,5] *N*,*N*- or *C*,*N*-malononitrilato,[6] acetonyl,[7] hydrosulfide,[8] and triazenide[9] complexes have also been prepared by reaction of hydroxo complexes with ROH, RNH_2, $CH_2(CN)_2$, Me_2CO, H_2S or RN═NNHR (R = aryl), respectively. No intermediate aqua complex has been detected in these acid−base reactions [M−OH + H^+X^- → (M−OH_2)$^+$ + X^- → M−X + H_2O], but palladium aqua complexes have been prepared when a palladium hydroxo complex is treated with triflic acid,[10] owing to the noncoordinating ability of triflate, (CF_3SO_3)$^-$. Pentacoordinate nickel(II) complexes[11] contain-

* Authors to whom correspondence should be addressed. Fax: (+34) 968 36 41 48. E-mail: jruiz@um.es (J.R.); gll@um.es (G.L.).

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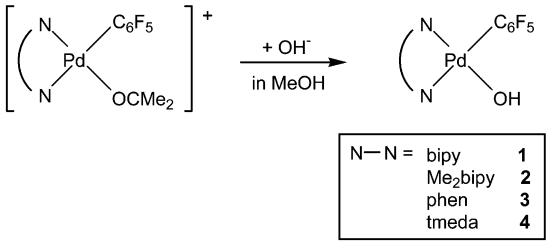
ing N,S-donor and hydroxamate ligands have also been prepared starting from the hydroxo complex $[Ni_2(macrocycle)_2(\mu\text{-}OH)_2]^{2+}$. The synthesis and dehydrative condensation of complexes [(Tp)(py)Pd(OH)] and $[\{(Tp)(H_2O)Pd\}_2(\mu\text{-}OH)_2]$ (Tp = hydrotris(3,5-diisopropylpyrazolyl)borato) have also been reported.[12]

In the reaction of $[M_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ with amines in the presence of CS_2 to form dithiocarbamate complexes (M = Pd, Pt),[2a] it was suggested that after deprotonation of the amine by the hydroxo complex to give an intermediate amido complex there was insertion of CS_2 into the M−N bond to give the dithiocarbamate complex. In fact, the amido complex $[Pd_2(C_6F_5)_4(\mu\text{-}NHPh)_2]^{2-}$ reacts with CS_2, yielding the *N*-phenyldithiocarbamate complex $[M(C_6F_5)_2(S_2CNHPh)]^-$.[6b] We have now investigated the chemical behavior of the new monomeric complexes $[Pd(N{-}N)(C_6F_5)(OH)]$ toward CO, CO_2, PhNCS, and PhCNO. The insertion of CO into a Pd−OMe bond is one of the fundamental steps in various palladium-catalyzed organic reactions such as the hydroesterification of alkenes.[13]

Scheme 1



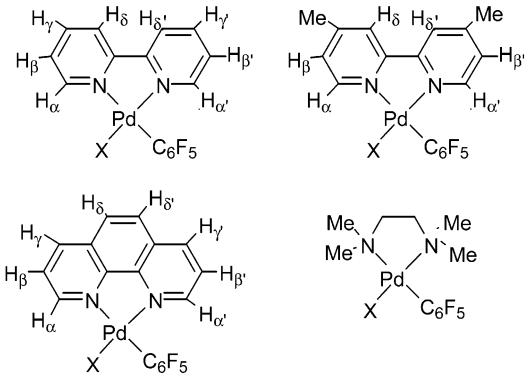
Results and Discussion

Mononuclear Hydroxo Complexes $[Pd(N{-}N)(C_6F_5)(OH)]$. In methanol, the complexes $[(N{-}N)(C_6F_5)Pd(Me_2CO)]ClO_4$ [N−N = bipy (2,2′-bipyridyl), Me_2bipy (4,4′-dimethyl-2,2′-bipyridyl), phen (1,10-phenanthroline), or tmeda (tetramethylethylenediamine)] react with KOH to yield the corresponding neutral hydroxo complexes $[(N{-}N)(C_6F_5)Pd(OH)]$ (**1**−**4**) (Scheme 1) in 75−88% yields. Although binuclear μ-methoxo complexes were obtained by treating μ-hydroxo complexes with methanol[1d] and *trans*-$[Pd(PPh_3)_2(C_6F_5)(OCH_3)]$ has also been reported,[14] no methoxo compound was isolated in these reactions. The structures for the pale yellow complexes **1**−**4** were assigned on the basis of microanalytical, IR, and ^1H and ^{19}F NMR data.

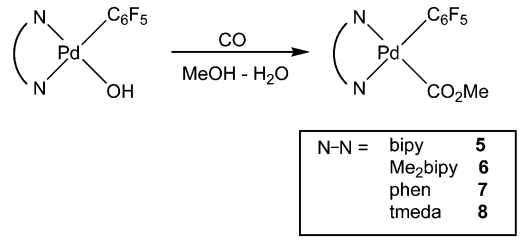
The IR spectra of complexes **1**−**4** show the characteristic absorptions of the C_6F_5 group[15] at ca. 1630, 1490, 1450, 1050, 950, and 790 cm^{-1}. The latter absorption derives from the so-called "X-sensitive" mode in C_6F_5–X molecules,[16] and it is observed as a single band, as expected from the presence of only one C_6F_5 group in the coordination sphere of the palladium atom.[17−19] A band found at 3610−3605 cm^{-1} in the IR spectra is assigned to ν(OH). The presence of the hydroxo ligand is also established by the observation of a high-field proton resonance (δ −0.75 to −2.00) which is in accord with the results observed for hydroxo complexes of the group 10 elements.[1a,12] The characteristic resonances of the neutral ligands were also observed in the ^1H NMR spectra,[20−23] and the assignments presented in the Experi-

(1) (a) López, G.; García, G.; Ruiz, J.; García, J.; Vicente, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1046. (b) López, G.; Ruiz, J.; García, G.; Vicente, C.; Casabó, J.; Molins, E.; Miravitlles, C. *Inorg. Chem.* **1991**, *30*, 2605. (c) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 53. (d) López, G.; Ruiz, J.; García, G.; Vicente, C.; Rodríguez, V.; Sánchez, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1681. (e) López, G.; García, G.; Sánchez, G.; García, J.; Ruiz, J.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1992**, *31*, 1518. (f) Ruiz, J.; Vicente, C.; Martí, J. M.; Cutillas, N.; García, G.; López, G. *J. Organomet. Chem.* **1993**, *460*, 241. (g) Ruiz, J.; Cutillas, N.; Torregrosa, J.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1994**, 2353.
(2) (a) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Rodríguez, V. *J. Organomet. Chem.* **1992**, *436*, 121. (b) Sánchez, G.; Ruiz, F.; Santana, M. D.; García, G.; López, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1994**, 19. (c) Ruiz, J.; Rodríguez, V.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *J. Organomet. Chem.* **1995**, *493*, 77. (d) Ruiz, J.; Rodríguez, V.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *J. Organomet. Chem.*, **1996**, *523* , 23. (e) Sánchez, G.; Ruiz, F.; García, J.; Ramírez de Arellano, M. C.; López, G. *Helv. Chim. Acta* **1997**, *80* , 2477. (f) Ruiz, J.; Florenciano, F.; Sánchez, M. A.; López, G.; Ramírez de Arellano, M. C.; Pérez, J. *Eur. J. Inorg. Chem.* **2000**, 943.
(3) Ruiz, J.; Rodríguez, V.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1996**, *15*, 1662.
(4) (a) Ruiz, J.; Martínez, M. T.; Vicente, C.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321. (b) Ruiz, J.; Rodríguez, V.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1997**, 4271. (c) Ruiz, J.; Cutillas, N.; Torregrosa, J.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B.; Harrison, R. M. *J. Chem. Soc., Dalton Trans.* **1994**, 2353. (d) Ruiz, J.; Cutillas, N.; Sampedro, J.; López, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Organomet. Chem.* **1996**, *526*, 67.
(5) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4206.
(6) (a) López, G.; Sánchez, G.; García, G.; Ruiz, J.; García, J.; Martínez-Ripoll, M.; Vegas, A.; Hermoso, J. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 716. (b) Ruiz, J.; Rodríguez, V.; López, G.; Casabó, J.; Molins, E.; Miravitlles, C. *Organometallics* **1999**, *18*, 1177.
(7) Ruiz, J.; Rodríguez, V.; Cutillas, N.; Pardo, M.; Pérez, J.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **2001**, *20*, 1973.
(8) Ruiz, J.; Rodríguez, V.; Vicente, C.; Martí, J. M.; López, G.; Pérez, J. *Inorg. Chem.* **2001**, *40*, 5354.
(9) Ruiz, J.; López, J. F. J.; Rodríguez, V.; Pérez, J.; Ramírez de Arellano, M. C.; López, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2683.
(10) Ruiz, J.; Florenciano, F.; Vicente, C.; Ramírez de Arellano, M. C.; López, G. *Inorg. Chem. Commun.* **2000**, *3*, 73.
(11) (a) Santana, M. D.; García, G.; Rufete, A.; Ramírez de Arellano, M. C.; López, G. *J. Chem. Soc., Dalton Trans.* **2000**, 619. (b) Santana, M. D.; García, G.; Pérez, J.; Molins, E.; López, G. *Inorg. Chem.* **2001**, *40*, 5701.
(12) Akita, M.; Miyaji, T.; Muroga, N.; Mock-Knoblauch, C.; Adam, W.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **2000**, *39*, 2096.
(13) (a) Cavinato, G.; Vavasori, A.; Toniolo, L.; Benetollo, F. *Inorg. Chim. Acta* **2003**, *343*, 183. (b) Huh, K.-T, Alper, H. *Bull. Korean Chem. Soc.* **1994**, *15*, 304. (c) Kapteijn, G. M.; Verhoef, M. J.; van den Broek, F. H.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1995**, *503*, C26. (d) Bertoux, F.; Castanet, Y.; Civade, E.; Monflier, E.; Mortreux, A. *Catal. Lett.* **1998**, *54*, 199.
(14) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.
(15) Long, D. A.; Steel, D. *Spectrochim. Acta* **1963**, *19*, 1955.
(16) Maslowski, E. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 437.
(17) Alonso, E.; Forniés, J.; Fortuño, C.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3777.
(18) López, G.; Ruiz, J.; Vicente, C.; Martí, J. M.; García, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1992**, *11*, 4091.
(19) Ruiz, J.; Martínez, M. T.; Vicente, C.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321.
(20) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210.
(21) Fuchita, Y.; Harada, Y. *Inorg. Chim. Acta* **1993**, *208*, 43.
(22) Smith, G. D.; Hanson, B. E.; Merola, J. S.; Waller, F. J. *Organometallics* **1993**, *12*, 568.
(23) Forniés, J.; Martínez, F.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **1995**, *495*, 185.

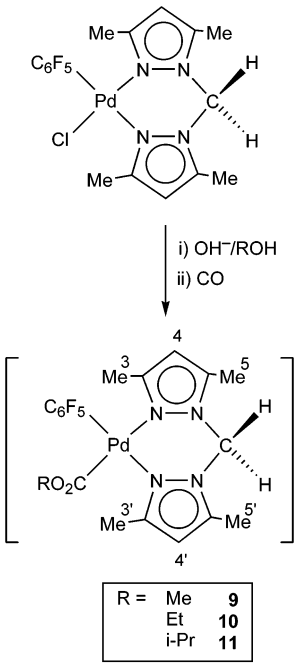
Scheme 2



Scheme 3



Scheme 4



mental Section are based on the atom numbering given in Scheme 2. The low-field resonance (δ 8.8−9.3) is assigned to the α-H atom,[23] and the assignment of the signals found in the range 9.3−7.01 was confirmed by the ^{1}H−^{1}H COSY spectrum of complex **3**. The ^{19}F NMR spectra show the expected three resonances for $2F_o$:$1F_p$:$2F_m$ of the C_6F_5 ligand.

Alkoxycarbonyl Complexes [(N−N)Pd(C_6F_5)(CO_2R)]. Only a few palladium methoxycarbonyl complexes have been prepared; these include [(bipy)Pd(CO_2Me)$_2$],[23] [(PPh_3)$_2$PdCl(CO_2Me)],[24,25] [(PPh_3)$_2$Pd(CO_2Me)$_2$],[26] [(PPh_3)$_2$Pd(OAc)(CO_2Me)],[27]and [(PMe_3)$_2$Pd(CH_2Ph)(CO_2Me)].[28] Others have been detected by NMR spectroscopy, but they could not be isolated: [(P−P)(PPh_3)Pd(CO_2Me)](SO_3CF_3),[29] [(P−P)PdMe(CO_2Me)],[30] and [(P−P)PdMe{$CO_2CH(CF_3)_2$}].[31]The carbonylation of [(PPh_3)$_2$Pd$_2$(C_6H_5)$_2$(μ-OH)$_2$] in the presence of PhI has been reported.[32]

When CO is bubbled through a solution of the monomeric hydroxo complexes **1**−**4** in methanol at room temperature for 5−15 min, the methoxycarbonyl complexes [(N−N)(C_6F_5)Pd(CO_2Me)] (**5**−**8**) are obtained in 55−80% yields (Scheme 3). Complexes **5**−**8** are all air-stable solids, and the thermal analysis shows that they decompose above 140 °C in a dynamic N_2 atmosphere. A very strong band in the IR spectra at ca. 1650 cm^{-1} is assigned to ν(CO). The resonance signal observed in the ^{1}H NMR spectra at ca. 3.50 ppm is due to the CO_2Me protons. The CO resonance of the methoxycarbonyl ligand of complexes **5**−**7** could not be observed in the ^{13}C NMR spectra because of their low solubility, but it was observed in $CDCl_3$ solution for the more soluble complex **8** as a triplet signal at δ 183.6 due to coupling to the *o*-fluorine atoms of the C_6F_5 group [$^4J(CF_o)$ = 5.4 Hz].

When CO is bubbled through an alcoholic (MeOH, EtOH, ^{i}PrOH) solution of [(N−N)Pd(C_6F_5)(OH)] [N−N = bis(3,5-dimethylpyrazol-1-yl)methane], generated in situ by the addition of KOH to the complexes [(N−N)Pd(C_6F_5)Cl], the corresponding bis(pyrazol-1-yl)methane complexes [(N−N)Pd(C_6F_5)(CO_2R)] [R = Me (**9**), Et (**10**), or ^{i}Pr (**11**)] are obtained (Scheme 4).

The IR spectra of complexes **9**−**11** show a band at ca. 1640 cm^{-1} which is assigned to ν(CO), and a single band located at 790 cm^{-1} is indicative of the presence of only one C_6F_5 group in the coordination sphere of the palladium atom. Two sets of ^{1}H resonances are observed for the $C_3HMe_2N_2$ rings corresponding to one pyrazolate ligand *trans* to CO_2R and one pyrazolate ligand *trans* to C_6F_5; the lower field set is assigned to the pyrazolate ligand *trans* to C_6F_5 (Scheme 4). The ^{19}F NMR spectra of complexes **9**−**11** at room temperature show the expected three resonances for the C_6F_5 ligand, but those derived from the *o*-fluorine atoms are observed as broad signals. Furthermore, the proton resonances of the bridging methylene chain of the bis(pyrazol-1-yl)methane ligand and some of the proton resonances of the OR groups appear as broad signals too. A number of studies have been performed on bis(pyrazolyl)methane ligands coordinated to a metallic center,[33]and it is found that the two conformers shown in Figure 1 may be in

(24) Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* **1993**, *444*, C65.
(25) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180.
(26) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686.
(27) Caglio, G. *J. Chem. Soc. A* **1970**, 1836.
(28) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817.
(29) Dekker: G. P. C. M.; Elsevier: C. J.; Vrieze, K.; Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357.
(30) Toth, I.; Elsevier: C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 529.
(31) Kim, Y.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182.
(32) Grushin, V. V.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4305.
(33) Byers, P. K.; Canty, A. J.; Honeyman, R. T. *Adv. Organomet. Chem.* **1992**, *34*, 1.

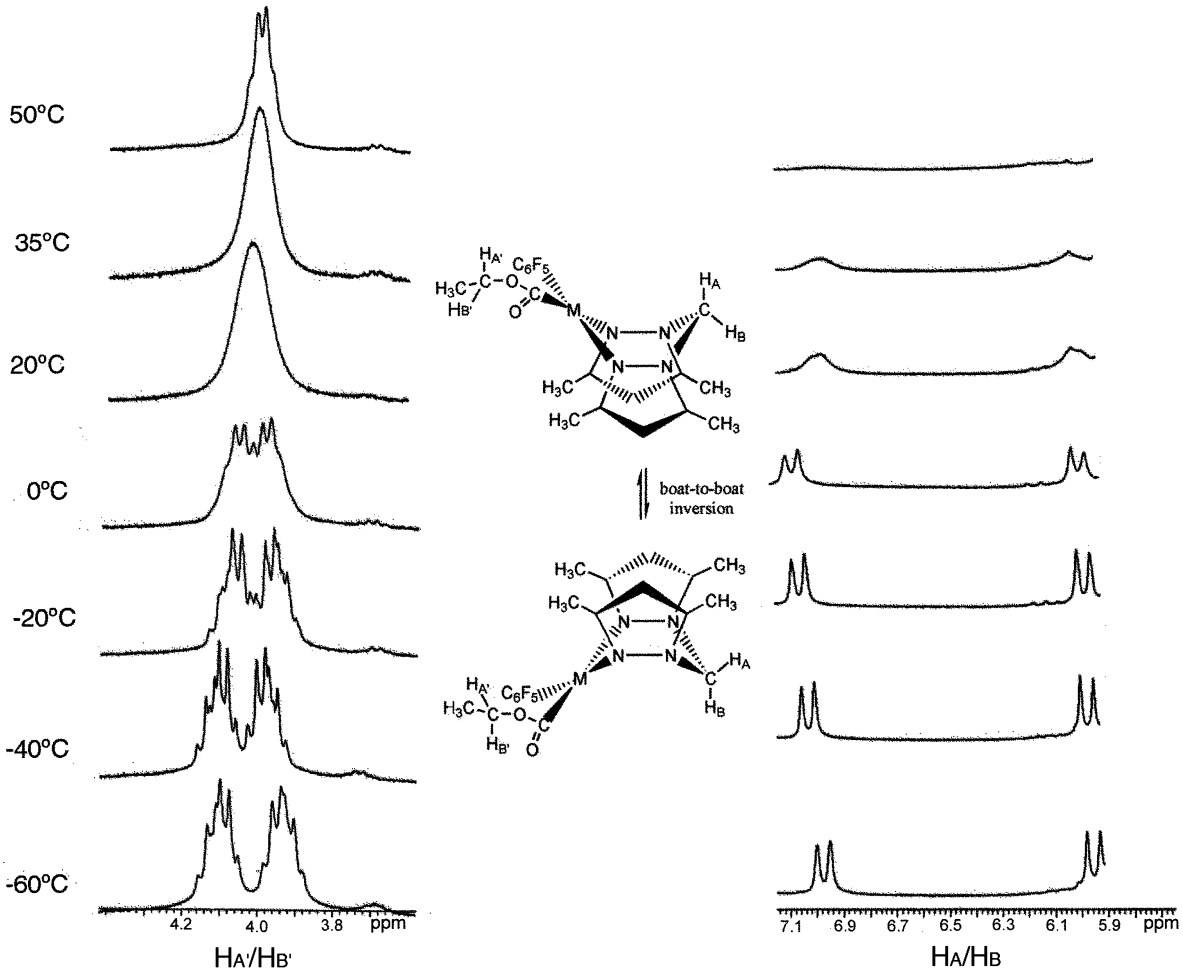


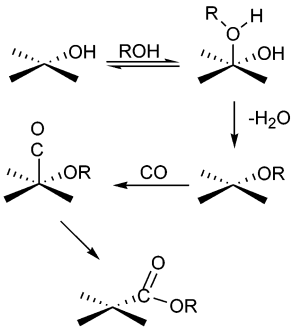
Figure 1. Variable-temperature ^{1}H NMR spectra of [Pd{$CH_2(C_3HMe_2N_2)_2(C_6F_5)$}{C(O)OEt}] in the C−$CH_2$−O (left) and N−$CH_2$−N (right) regions, and the boat-to-boat inversion of the metallacycle Pd(N−N)$_2$C.

a chemical exchange through a boat-to-boat inversion. The variable-temperature ^{1}H NMR spectrum of complex **10** (Figure 1) provides cogent evidence for the existence of the aforementioned inversion of the metallacycle ring. At low temperatures, when the inversion is frozen, protons A and B are magnetically nonequivalent and give the expected NMR pattern corresponding to two diastereotopic protons: two doublets with $^2J(H_AH_B) = 15$ Hz that collapse at 50 °C. At lower temperatures two methylene resonances are also observed for protons A′ and B′; each signal is observed as a doublet ($^2J(H_{A'}H_{B'})$ of quartets ($^3J(CH_3/H_{A'}$ or $H_{B'})$) with the quartets partly overlapped owing to accidental coincidence of the two coupling constants. At higher temperatures the $H_{A'}$ and $H_{B'}$ resonances coalesce, and at 50 °C the resolution of the splitting between CH_3 and CH_2 is already discernible in the spectrum.

The formation of complexes **5**−**11** is formally the insertion of CO into the Pd−OR bond. Although no alkoxo complexes have been isolated, they probably are formed in the alcoholic solution, and a carbonyl insertion into Pd−OMe could be a possible pathway to the formation of M−CO_2R. The existence of an intermediate methoxopalladium complex was shown by the following experiment. [(N−N)Pd(C_6F_5)Cl] was treated with 1 equiv of $AgClO_4$ in acetone, and the suspension was filtered to remove the precipitated AgCl. The solution was then evaporated under vacuum to dryness, and 1 equiv of KOH in methanol was added to the residue. The solution was again evaporated to dryness and the residue extracted with dichloromethane. Filtration, concentration under vacuum, and addition of hexane gave a solid that was investigated by ^{1}H NMR spectroscopy in the solvent $CDCl_3$. The ^{1}H spectrum (only the MeO and Me proton signals are given below) showed that the product was a mixture of [(N−N)Pd(C_6F_5)(OMe)] [δ 3.08 (s, 3H, MeO), 2.55 (s, 3H, Me3′), 2.37 (s, 6H, Me5 + Me5′), 1.83 (s, 3H, Me3)] and [(N−N)Pd(C_6F_5)(OH)] [δ 2.59 (s, 3H, Me3′), 2.38 (s, 6H, Me5 + Me5′), 1.81 (s, 3H, Me3)] together with small amounts of six unidentified palladium species. The relative intensities of the proton signals indicated a mole ratio of methoxo complex to hydroxo complex ≅2:1. The observation of the Pd−OMe signal at δ 3.08 is in agreement with the values found in [(PPh_3)$_2$Pd(C_6F_5)(OMe)] (δ 3.08)[14] and [(*o*-$Ph_2PC_6H_4CH{=}N^iPr$)Pd(C_6F_5)(OMe)] (δ 3.4).[34] The Pd−OH signal, which should be found at high field between −2 and −3 ppm,[1b,14] could not be observed in the ^{1}H spectrum, but the infrared spectrum of the solid in Nujol mull showed a sharp ν(OH) band at 3605 cm^{-1}. Attempts made to isolate

(34) Sánchez, G.; Serrano, J. L.; Momblona, F.; Ruiz, F.; García, J.; Pérez, J.; López, G.; Chaloner, P. A.; Hitchcock, P. *Polyhedron* **2001**, *20*, 571.

Scheme 5



pure samples of the hydroxo or the methoxo complexes were unsuccessful.

Carbonyl insertion into a M−OMe bond has been demonstrated to occur in [(dppe)PtMe(OMe)], which reacts with CO at room temperature to yield [(dppe)Pt(Me)(CO_2Me)],[26] and the formation of the iridium carbomethoxy complex [(PPh_3)$_2$(CO)$_2$Ir(CO_2Me)] by nucleophilic attack on coordinated CO by methoxide has been reported,[35] as well as the reaction of the cationic complex *trans*-[(PPh_3)$_2$Pt(C_6F_5)(CO)]-BF_4 with methanol to give the methoxycarbonyl complex *trans*-[(PPh_3)$_2$Pt(C_6F_5)(CO_2Me)].[36] Van Koten[37] has suggested a dissociative mechanism with displacement of RO^- by CO to form a cationic carbonyl complex followed by nucleophilic attack of the methoxide anion on coordinated CO. The reaction of CO with bis(μ-aryloxo) complexes [(C_6F_5)$_2$M(μ-OR)$_2$(C_6F_5)$_2$]$^{2-}$ (M = Pd, Pt)[16] has also been studied and leads to the formation of [(C_6F_5)$_2$M(OR)(CO)]$^-$. Detailed mechanistic information on the carbonylation reactions of [(diphos)PtMe(OMe)]-type complexes indicates that these reactions are best described as inner-sphere migratory insertions involving precoordination of CO to the metal center to generate a 5-coordinate intermediate.[38] In fact, (i) no reaction was observed when CO was bubbled through a solution of **1** in tetrahydrofuran, and (ii) when NaOMe was added to a solution of the previously reported carbonyl complex[(bipy)(C_6F_5)Pd(CO)]ClO_4[39] in methanol, we obtained the neutral methoxycarbonyl complex [(bipy)-(C_6F_5)Pd(CO_2Me)] (**5**). According to the literature and experimental data, the mechanism shown in Scheme 5 may be proposed, although the alternative mechanism based on the nucleophilic attack by external RO^- on coordinated CO cannot be discarded.

Crystal Structure of 8. Colorless crystals suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a benzene solution of **8**. The crystal structure of complex **8** is shown in Figure 2. The coordination around Pd is distorted square-planar. The different Pd−N (Pd−N(1),

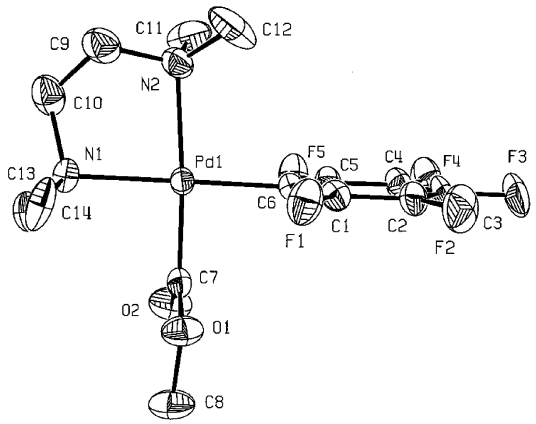
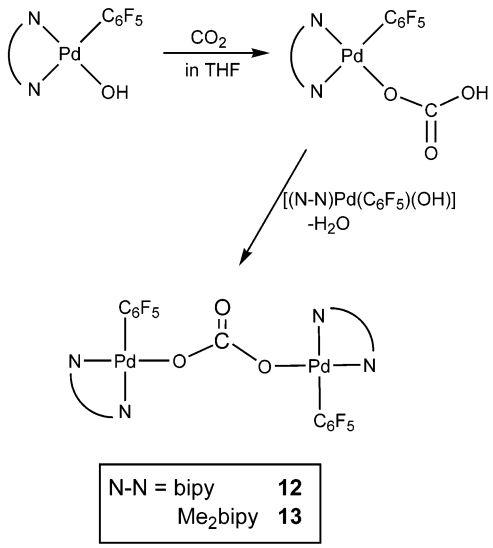


Figure 2. Crystal structure of **8**. Selected bond lengths (Å): Pd−N(1) 2.139(5), Pd−N(2) 2.176(6), Pd−C(6) 2.019(6), Pd−C(7) 1.961(6), C(7)−O(1) 1.329(8), C(7)−O(2) 1.199(8).

Scheme 6



2.139(5) Å; Pd−N(2), 2.176(6) Å) distances are in agreement with the higher *trans* influence of the CO_2Me group compared to C_6F_5. The CO_2Me group is planar, and the Pd−CO_2Me distance (1.961(6) Å) is shorter than that found in [(bipy)Pd(CO_2Me)$_2$] (1.989(9) Å).[22] The C(7)−O(1) distance of the CO_2Me group (1.329(8) Å) is typical of a single bond, and the C(7)−O(2) distance (1.199(8) Å) is representative of double carbon−oxygen bonds.[22] The Pd−C_6F_5 bond length (2.019(6) Å) is in the range found in the literature for (pentafluorophenyl)palladium complexes.[23] The chelate angle N(1)−Pd−N(2) (83.9(2)°) is similar to that found (84.8(5)°) in [{Pd(tmeda)}$_2$(μ-OH)(μ-HNC_6H_4Cl-*p*)]$^{2+}$.[40]

Carbonate Complexes. When CO_2 is bubbled through a suspension of the monomeric hydroxo complex **1** or **2** in tetrahydrofuran (**1**) or dichloromethane (**2**) at room temperature for 5 min, the binuclear carbonate complexes [(N−N)(C_6F_5)Pd(μ-CO_3)Pd(C_6F_5)(N−N)] (N−N = bipy (**12**) or Me_2bipy (**13**)) are obtained (Scheme 6). The IR spectra of both compounds display strong absorptions at 1540 and 1300 cm^{-1} due to the $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ vibrational modes

(35) Rees, M. W.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179.
(36) Cherwinski, W. J.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 2263.
(37) Kapteijn, G. M.; Dervisi, A.; Verhoef, M. J.; van den Broek, M. A. F. H.; Grove, D. M.; van Koten, G. *J. Organomet. Chem.* **1996**, *517*, 123.
(38) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163 and references therein.
(39) Usón, R.; Fornies, J.; Martínez, F. *J. Organomet. Chem.* **1976**, *112*, 105.
(40) Sánchez, G.; Serrano, J. L.; García, J.; López, G.; Pérez, J.; Molins, E. *Inorg. Chim. Acta* **1999**, *287*, 37.

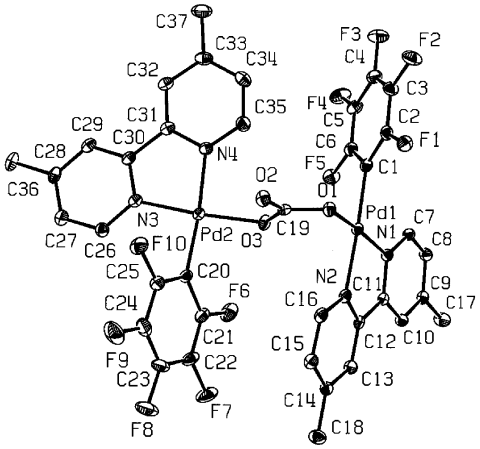


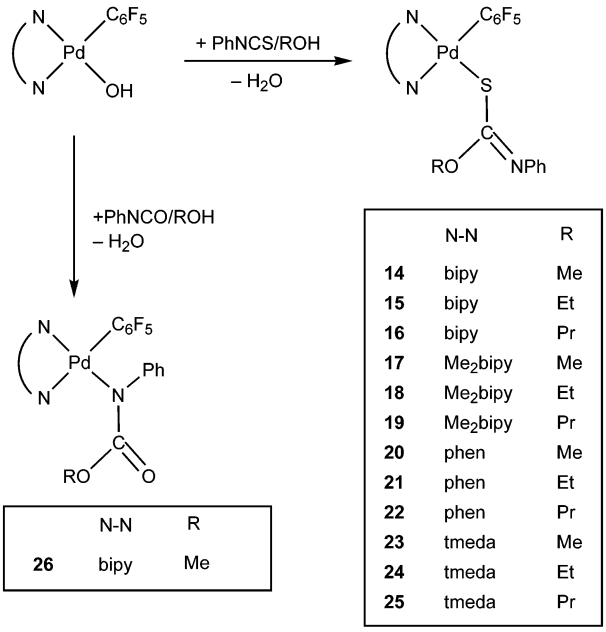
Figure 3. Crystal structure of **13.** Selected bond lengths (Å): Pd(1)−O(1) 2.014(2), Pd(2)−O(3) 1.995(2), C(19)−O(1) 1.309(4), C(19)−O(3) 1.308(4), C(19)−O(2) 1.235(4). Angle (deg) between the coordination planes of Pd(1) and Pd(2): 66.54(8).

of the carbonate ligand, respectively.[41−43] The crystal X-ray structure of the related carbonato complex of rhodium, $[(C_6F_5)Rh(\mu\text{-}CO_3)Rh(C_6F_5)]^{2-}$, has been reported,[43] and monometallic bis(hydrogen carbonato) complexes of palladium of the types $[Pd\{OC(O)OH\}_2L_2]$ and $[Pd\{OC(O)OH\}_2(L-L)_2]$ have been prepared by insertion of carbon dioxide into palladium−hydroxide bonds.[44] However, the recently reported [Pd(TMEDA)(η^2-CO_3)] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was isolated by reacting $[Pd(TMEDA)(OC_6H_4{}^tBu\text{-}p)_2]$ with CO_2 in the presence of water.[45]

The insertion of CO_2 into the Pd−OH bond, perhaps via the formation of a pentacoordinate intermediate, $[(N-N)Pd(C_6F_5)(CO_2)(OH)]$, should give the hydrogen carbonato complexes $[(N-N)Pd(C_6F_5)\{OC(=O)OH\}]$, and the carbonato complexes **12** and **13** should be subsequently formed via the acid−base reaction between the hydrogen carbonato complexes and the unreacted hydroxo complex as shown in Scheme 6.

Crystal Structure of 13. Crystals suitable for structural determination were obtained by slow diffusion of hexane into a dichloromethane−toluene solution of complex **13**. The crystal structure of **13** is shown in Figure 3. So far as we aware this is the first carbonate-bridged palladium species to be structurally characterized [3D search using the Cambridge Structural Database, April 2002 release]. The structure shows the planar carbonate anion acting as a symmetric bridging bidentate ligand to both palladium(II) centers. The mean plane defined by the carbonate group and the two palladium atoms is close to planar with a maximum deviation of 0.1 Å [O(3)]. The coordination planes of the two Pd atoms

Scheme 7



	N-N	R
26	bipy	Me

	N-N	R
14	bipy	Me
15	bipy	Et
16	bipy	Pr
17	Me_2bipy	Me
18	Me_2bipy	Et
19	Me_2bipy	Pr
20	phen	Me
21	phen	Et
22	phen	Pr
23	tmeda	Me
24	tmeda	Et
25	tmeda	Pr

make an interplanar angle of 66.54(8)°. The Pd(1)−O(1) and Pd(2)−O(3) bond distances (2.014(2) and 1.995(2) Å, respectively) are shorter than the Pt−O distance of 2.087(7) Å reported for the carbonatoplatinum complex $[(PBz_3)_4Pt_2(Ph)_2(\eta^1,\eta^1,\mu\text{-}CO_3)(toluene)]$,[42] the Pd−O distance of 2.114(3) Å reported for the monometallic bis(hydrogen carbonato)-palladium complex $[Pd(OCO_2H)_2(dppe)]$,[44] and the Rh−O distance of 2.154(9) Å found in the dimeric carbonato-rhodium complex $[\{(C_6F_5)_3Rh\}_2(\mu\text{-}CO_3)]^{2-}$,[43] but they are comparable with the Pd−O distance found in [Pd(TMEDA)-(η^2-CO_3)].[45] The C(19)−O(1) (1.309(4) Å) and C(19)−O(3) (1.308(4) Å) bond lengths in the carbonate complex **13** are comparable with those observed for $[(PBz_3)_4Pt_2(Ph)_2(\eta^1,\eta^1,\mu\text{-}CO_3)(toluene)]$ (1.29(1) Å).[42] On the other hand, the C(19)−O(2) bond distance (1.235(4) Å) is shorter than the C(19)−O(1) and C(19)−O(3) ones. The different Pd−N distances (Pd(1)−N(1), 2.028(3) Å; Pd(1)−N(2), 2.067(3) Å; Pd(2)−N(3), 2.024(3) Å; Pd(2)−N(4), 2.063(3) Å) are in agreement with the higher *trans* influence of the C_6F_5 group compared to the carbonato ligand. The Pd−C_6F_5 distances are similar to those found in complex **8** and in the literature.[23] The chelate angles N(1)−Pd(1)−N(2) and N(3)−Pd(2)−N(4) (80.04(11)° and 80.22(11)°, respectively) are smaller than those found in complex **8**.

Carbamate and Thiocarbamate Complexes. We have demonstrated that in the reaction of amines with hydroxo-bridged nickel(II), palladium(II), and platinum(II) complexes in the presence of carbon disulfide, C−N bonds are formed to give *N*,*N*-dialkyldithiocarbamate complexes.[2a,46]

The hydroxopalladium complexes **1**−**4** react with PhNCS in alcohol (MeOH, EtOH, or PrOH) at room temperature, yielding the corresponding *N*-phenyl-*O*-alkylthiocarbamate metal complexes $[(N-N)Pd(C_6F_5)\{SC(=NPh)OR\}]$ (**14**−**25**) (Scheme 7).

(41) Carmona, E.; Marín, J. M.; Palma, P.; Paneque, M.; Poveda, M. L. *Inorg. Chem.* **1989**, *28*, 1895.
(42) Michelin, R. A.; Strukul, G.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L. *Inorg. Chim. Acta* **1984**, *84*, 229.
(43) García, M. P.; Jiménez, M. V.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1995**, 917.
(44) Ganguly, S.; Mague, J. T.; Roundhill D. M. *Inorg. Chem.* **1992**, *31*, 3831.
(45) Yasuda, H.; Choi, J.-C.; Lee, S.-C.; Sakakura, T. *Organometallics* **2002**, *21*, 1216.
(46) López, G.; Sánchez, G.; García, G.; García, J.; Sanmartín, A.; Santana, M. D. *Polyhedron* **1991**, *10*, 2821.

The IR spectra of compounds **14**−**25** show the characteristic absorptions of the C_6F_5 group at 1630, 1490, 1450, 1050, and 950 cm^{-1} and a single band at ca. 800 cm^{-1} for the X-sensitive mode. The observation of the ν(C═N) vibration at ca. 1580 cm^{-1} suggests that the thiocarbamate ligand is coordinated to the metal through the S atom. The ^{1}H NMR spectra show the characteristic resonances of the neutral N−N ligand[20] and the *N*-phenyl-*O*-alkylthiocarbamate group. The observation of three or two signals for the aromatic protons of the PhN groups indicates that rotation of the aryl group about the C−N bond is rapid on the NMR time scale. The ^{19}F NMR spectra of complexes **14**−**25** reveal a freely rotating pentafluorophenyl ring which gives the expected three resonances in the ratio 2:1:2 for the *o*-, *p*-, and *m*-fluorine atoms, respectively.

The hydroxopalladium complex **1** also reacts with PhNCO in methanol solution at room temperature to yield the *N*-phenyl-*O*-methylcarbamato complex [(bipy)Pd(C_6F_5)-{NPhC(O)OR}] (**26**) (Scheme 7). The reaction between *trans*-[PtH(OPh)(PEt_3)$_2$] and phenyl isocyanate, PhNCO, to give the *N*,*O*-diphenylcarbamato complex *trans*-[PtH{PhNC-(O)Ph}(PEt_3)$_2$], where phenyl isocyanate inserts cleanly into the platinum−oxygen bond, has been reported,[47] but the related nickel complex *trans*-[NiH(PhNC(O)OPh)(PEt_3)$_2$], although detected by ^{1}H NMR, could not be isolated because a reversible insertion reaction occurs.[48] Insertion of PhNCO into the metal−oxygen bond of *fac*-[$(CO)_3$(dppe)M(OMe)] (M = Mn or Re) has also been reported.[49] The ^{19}F NMR spectrum of complex **26** reveals that rotation of the pentafluorophenyl ring around the Pd−C_6F_5 bond is hindered. Instead of the three resonances with relative intensities of $2F_o$:$1F_p$:$2F_m$ expected for a freely rotating C_6F_5 ring, four 1:1:1:1 resonance signals are observed in the *o*- and *m*-fluorine atom regions. This experimental observation is in agreement with the coordination of the carbamate ligand through the N atom. The phenyl group at the N atom lies adjacent to the C_6F_5 ring, preventing its free rotation.

The formation of complexes **14**−**25** and **26** is the result of the insertion of PhNCS or PhNCO into the corresponding Pd−OR bond. As with the formation of the alkoxycarbonyl derivatives aforementioned, preformation of an alkoxometal intermediate followed by insertion of the heterocumulene or external attack by RO^- of the coordinated heterocumulene is an alternative pathway to the formation of **14**−**26**.

Crystal Structure of 23. Crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a benzene solution of **23**. The crystal structure of complex **23** is shown in Figure 4. The donor atoms and the metal are coplanar (maximum deviation of 0.01 Å). The thiocarbamate group is not exactly planar, the C(1) atom being 0.02 Å out of the plane of the three bonded atoms S, O(1), and N(1). The N(1)−C(19) bond length (1.265(5) Å) and the C(19)−N(1)−C(1) angle (122.5(3)°) indicate that N(1) is sp^2-hybridized and that a high N−C double bond

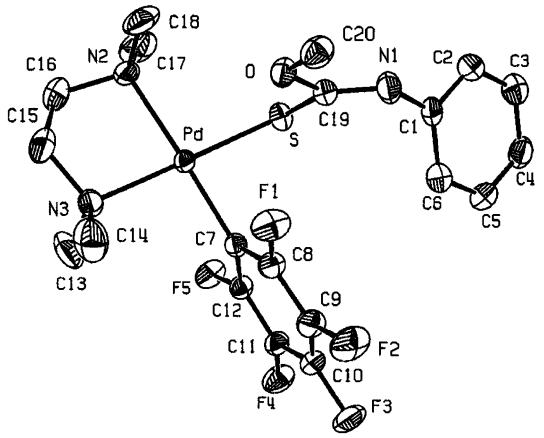
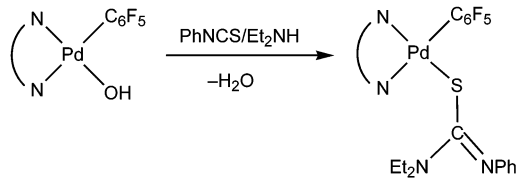


Figure 4. Crystal structure of **23**. Selected bond lengths (Å) and angles (deg): Pd−S 2.3099(10), Pd−C(7) 2.022(3), Pd−N(2) 2.153(3), Pd−N(3) 2.123(3), C(19)−N(1) 1.265(5), C(19)−N(1)−C(1) 122.5(3).

Scheme 8



	N-N
27	bipy
28	Me_2bipy
29	phen
30	tmeda

character exists.[50] Bond angles around the C(19) atom (128−112°) and the total of the surrounding three bond angles (359.9°) also clearly confirm the sp^2 hybridization of the C(19) atom. The Pd−S bond distance (2.3099(10) Å) is a little shorter than those found in [Pd(C_6F_5)(SC_6H_5)(*o*-$Ph_2PC_6H_4CHN^iPr$)] (2.357(2) Å)[51] and [($CH_2CH_2CH_2CH_2$-NCS_2)Pd(PEt_3)(^{n}Pr)] (2.384(2) and 2.406(1) Å),[52] and similar to those found in [$Pd_3(Et_2NCS_2)_4Cl_2$].[53] The Pd−C_6F_5 distance (2.022(3) Å) and the chelate angle N(3)−Pd−N(2) (83.96(12)°) are similar to those found in complex **8**. The different distances Pd−N (Pd−N(2), 2.153(3) Å; Pd−N(3), 2.123(3) Å) are in agreement with the higher *trans* influence of the C_6F_5 group compared with the thiocarbamate ligand.

Thioureide Complexes. The hydroxopalladium complexes **1**−**4** react with PhNCS in the presence of Et_2NH, affording the thioureidopalladium complexes [(N−N)Pd(C_6F_5)-($NPhCSNR_2$)] (**27**−**30**) (Scheme 8). In this case, the reaction between Et_2NH and the hydroxopalladium complex should give the amide complex [(N−N)Pd(C_6F_5)(Et_2N)] followed by insertion of PhNCS into the Pd−NEt_2 bond. The crystal

(47) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750.
(48) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371.
(49) Mandal, S. K.; Ho, D. M.; Orchin, M. *Organometallics* **1993**, *12*, 1714.
(50) Lappert, M. F.; Pye, P. L.; McLaughlin, G. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1272.
(51) Sánchez, G.; Serrano, J. L.; Momblona, F.; Ruiz, F.; García, J.; Pérez, J.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Polyhedron* **2001**, *20*, 571.
(52) Reger, D. L.; Garza, D. G.; Lebioda, L. *Organometallics* **1991**, *10*, 902.
(53) Sokolov, M.; Imoto, H.; Saito, T. *Inorg. Chem. Commun.* **1999**, *2*, 422.

structure of the thioureido derivative [Rh(C_5Me_5)Cl{PhNC-[N(C_6H_4Me-*p*)CH═NC_6H_4Me-*p*]S}] arising from the insertion of PhNCS into the Rh−N bond has been reported.[54] The molecule contains the four-membered chelate ring Rh−N−C−S. The C−N and C−S bonds have a considerable double bond character with a higher percentage for the former. The IR spectra of complexes **27**−**30** show the characteristic absorptions of the C_6F_5 ligand and a strong absorption at 1555−1535 cm^{-1} which is in the range found for the few thioureido complexes reported[54] and is dependent on the double bond character of the C−N bond. The ^1H NMR spectra show the resonance signals of the N−N ligands and the Et_2N and PhN groups, and the ^{19}F NMR spectra show the expected three signals with relative intensities of $2F_o$: $1F_p$:$2F_m$ corresponding to the C_6F_5 ligand.

Conclusion

(Alkoxycarbonyl)palladium complexes are readily obtained when CO is bubbled through an alcoholic solution of the mononuclear hydroxo complex [Pd(N−N)(C_6F_5)(OH)]. The reaction products are the result of the insertion of CO into the Pd−OR bond of alkoxypalladium intermediates that have not been isolated. These alkoxypalladium intermediates should be formed from the acid−base reaction between the hydroxopalladium complex and the corresponding alcohol (Pd−OH + ROH → Pd−OR + H_2O). With PhNCS and PhNCO, similar reactions occur and the corresponding thiocarbamate (Pd−SC(═NPh)OR) and carbamate (Pd−N(Ph)C(═O)OR) complexes are obtained. When, instead of ROH, Et_2NH is used as the nucleophile, the thioureide complex is formed: the insertion product of PhNCS into the Pd−NEt_2 bond (Pd−SC(═NPh)NEt_2). In the absence of a protic electrophile, insertion of CO_2 into the Pd−OH bond occurs and the hydrogen carbonate complex Pd−OC(═O)OH that should be formed reacts with the initial hydroxo complex to finally give the carbonato-bridged complex Pd−OC(═O)O−Pd. The X-ray diffraction studies of some of these complexes have been performed including the first crystal structure of a binuclear carbonatopalladium complex.

Experimental Section

Instrumental Measurements. The C, H, N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1} and the solid samples under nitrogen flow (100 mL min^{-1}). The NMR spectra were recorded on a Bruker AC 200E or Varian Unity 300 spectrometer, using $SiMe_4$ and $CFCl_3$ as standards, respectively. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Solvents were dried by the usual methods.

Materials. The starting complexes [(N−N)Pd(C_6F_5)(acetone)]ClO_4 (N−N = bipy, Me_2bipy, phen, and tmeda) were prepared by procedures described elsewhere.[39] The precursor [(N−N)Pd(C_6F_5)Cl] (N−N = bis(3,5-dimethyl-pyrazol-1-yl)methane) was prepared by the following method. To a solution of $[Pd_2(C_6F_5)_2(tht)_2(\mu\text{-}Cl)_2]$[55] (100 mg, 0.126 mmol; tht = tetrahydrothiophene) in dichloromethane (15 mL) was added bis(3,5-dimethyl-pyrazol-1-yl)methane (0.252 mmol). After being stirred at room temperature for 30 min, the solution was concentrated under vacuum, and hexane was added to give a yellow precipitate which was filtered off, air-dried, and characterized as [Pd(N−N)(C_6F_5)Cl]. Yield: 82%.

Preparation of Complexes [(N−N)Pd(OH)(C_6F_5)] (N−N = bipy (1), Me_2bipy (2), phen (3), or tmeda (4)). To a solution of the corresponding ionic perchlorate complex [(N−N)Pd(C_6F_5)-(acetone)]ClO_4 (0.96 mmol) in methanol (30 mL) was added KOH (2.00 mmol). The resulting solution was stirred for 1 h and concentrated under vacuum to dryness. The residue was treated with CH_2Cl_2, the precipitate was removed by filtration, and the filtrate was concentrated under vacuum. The addition of hexane caused the precipitation of a pale yellow solid which was collected by filtration and air-dried.

Data for Complex 1. Yield: 347 mg, 81%. Anal. Calcd for $C_{16}H_9N_2F_5OPd$: C, 43.0; H, 2.0; N, 6.3. Found: C, 42.8; H, 2.1; N, 6.1. Mp: 212 °C dec. IR (Nujol, cm^{-1}): ν(OH), 3610; ν(Pd−C_6F_5), 785. ^1H NMR ($CDCl_3$): δ($SiMe_4$) 9.00 (dd, 1H, H_α, $J(H_\alpha H_\beta)$ = 4.9 Hz, $J(H_\alpha H_\gamma)$ = 1.3 Hz), 8.00 (m, 5H, $H_{\alpha'}$ + H_γ + $H_{\gamma'}$ + H_δ + $H_{\delta'}$), 7.60 (dd, 1H, H_β, $J(H_\beta H_\gamma)$ = 8.2 Hz, $J(H_\alpha H_\beta)$ = 4.9 Hz), 7.26 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'})$ = 8.2 Hz, $J(H_{\alpha'}H_{\beta'})$ = 4.9 Hz), −0.90 (s, 1H, OH). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.1 (d, $2F_o$, $J(F_oF_m)$ = 21.4 Hz), −159.4 (t, $1F_p$, $J(F_mF_p)$ = 19.8 Hz), −162.5 (m, $2F_m$).

Data for Complex 2. Yield: 387 mg, 85%. Anal. Calcd for $C_{18}H_{13}N_2F_5OPd$: C, 45.5; H, 2.8; N 5.9. Found: C, 45.6; H, 2.7; N, 5.8. Mp: 247 °C dec. IR (Nujol, cm^{-1}): ν(OH), 3605; ν(Pd−C_6F_5), 790. ^1H NMR ($CDCl_3$): δ($SiMe_4$) 8.83 (d, 1H, H_α, $J(H_\alpha H_\beta)$ = 5.5 Hz), 7.79 (s, 2H, H_δ + $H_{\delta'}$), 7.68 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'})$ = 5.5 Hz), 7.34 (d, 1H, H_β, $J(H_\beta H_\alpha)$ = 5.5 Hz), 7.01 (d, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\alpha'})$ = 5.5 Hz), 2.44 (s, 3H, Me), 2.42 (s, 3H, Me), −0.92 (br, 1H, OH). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.2 (d, $2F_o$, $J(F_oF_m)$ = 21.4 Hz), −159.6 (t, $1F_p$, J (F_mF_p) = 20.0 Hz), −162.6 (m, $2F_m$).

Data for Complex 3. Yield: 398 mg, 88%. Anal. Calcd for $C_{18}H_9N_2F_5OPd$: C, 45.9; H, 1.9; N, 6.0. Found: C, 45.8; H, 2.0; N, 5.8. Mp: 234 °C dec. IR (Nujol, cm^{-1}): ν(OH), 3610; ν(Pd−C_6F_5), 790. ^1H NMR ($CDCl_3$): δ($SiMe_4$) 9.27 (dd, 1H, H_α, $J(H_\alpha H_\beta)$ = 4.9 Hz, $J(H_\alpha H_\gamma)$ = 1.3 Hz), 8.51 (dd, 1H, H_γ, $J(H_\beta H_\gamma)$ = 8.2 Hz, $J(H_\alpha H_\gamma)$ = 1.3 Hz), 8.43 (dd, 1H, $H_{\gamma'}$, $J(H_{\beta'}H_{\gamma'})$ = 8.2 Hz, $J(H_\alpha H_\gamma)$ = 1.3 Hz), 8.21 (dd, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'})$ = 4.9 Hz, $J(H_{\alpha'}H_{\gamma'})$ = 1.3 Hz), 7.91 (m, 3H, H_β + H_δ + $H_{\delta'}$), 7.60 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'})$ = 8.2 Hz, $J(H_{\alpha'}H_{\beta'})$ = 4.9 Hz), −0.75 (s, 1H, OH). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.1 (d, $2F_o$, $J(F_oF_m)$ = 21.4 Hz), −159.3 (t, $1F_p$, $J(F_mF_p)$ = 19.8 Hz), −162.5 (m, $2F_m$).

Data for Complex 4. Yield: 293 mg, 75%. Anal. Calcd for $C_{12}H_{17}N_2F_5OPd$: C, 35.4; H, 4.2; N, 6.9. Found: C, 35.2; H, 4.3; N, 6.6. Mp: 130 °C dec. IR (Nujol, cm^{-1}): ν(OH), 3610; ν(Pd−C_6F_5), 790. ^1H NMR ($CDCl_3$): δ($SiMe_4$) 2.68 (s, 6H, Me), 2.62 (m, 4H, CH_2), 2.45 (s, 6H, Me), −1.97 (br, 1H, OH). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.6 (d, $2F_o$, $J(F_oF_m)$ = 21.4 Hz), −160.1 (t, $1F_p$, $J(F_mF_p)$ = 19.8 Hz), −163.1 (m, $2F_m$).

Preparation of Complexes [(N−N)Pd(CO_2Me)(C_6F_5)] (N−N = bipy (5), Me_2bipy (6), phen (7), or tmeda (8)). A CO stream was passed through a solution of the corresponding hydroxo complex [(N−N)Pd(OH)(C_6F_5)] (0.130 mmol) in methanol (10 mL) for 5−15 min to give a white precipitate (for **5**−**7**) which was collected by filtration and air-dried. For the more soluble complex **8**, the resulting solution was concentrated under vacuum until

(54) Piraino, P.; Bruno, G.; Tresodi, G.; Faraone, G.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 2391.

(55) Usón, R.; Forniés, J.; Navarro, R.; García, M. P. *Inorg. Chim. Acta* **1979**, *33*, 69.

dryness and the residue was extracted with dichloromethane. Addition of hexane caused the precipitation of a solid which was collected by filtration and air-dried.

Data for Complex 5. Yield: 41 mg, 65%. Anal. Calcd for $C_{18}H_{11}N_2F_5O_2Pd$: C, 44.2; H, 2.3; N, 5.7. Found: C, 44.2; H, 2.1; N, 5.7. Mp: 209 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1635; ν(Pd−C_6F_5), 780. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.82 (d, H_α, $J(H_\alpha H_\beta)$ = 4.9 Hz), 8.04 (m, 4H, $H_\gamma + H_{\gamma'} + H_\delta + H_{\delta'}$), 7.83 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'})$ = 4.9 Hz), 7.50 (dd, H_β, $J(H_\beta H_\gamma)$ = 8.2 Hz, $J(H_\alpha H_\beta)$ = 4.9 Hz), 7.33 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'})$ = 8.2 Hz, $J(H_{\alpha'}H_{\beta'})$ = 4.9 Hz), 3.55 (s, 3H, OMe). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −115.5 (d, $2F_o$, $J(F_oF_m)$ = 21.6 Hz), −160.9 (t, $1F_p$, $J(F_mF_p)$ = 19.8), −163.1 (m, $2F_m$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ($SiMe_4$) 154.6−121.9 (CH of bipy), 51.14 (CH_3 of CO_2Me).

Data for Complex 6. Yield: 50 mg, 79%. Anal. Calcd for $C_{20}H_{15}N_2F_5O_2Pd$: C, 46.5; H, 2.9; N, 5.4. Found: C, 46.3; H, 3.0; N, 5.3. Mp: 204 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1655; ν(Pd−C_6F_5), 785. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.67 (d, 1H, H_α, $J(H_\alpha H_\beta)$ = 5.5 Hz), 7.86 (s, 1H, H_δ or $H_{\delta'}$), 7.83 (s, 1H, H_δ or $H_{\delta'}$), 7.67 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'})$ = 5.5 Hz), 7.30 (d, 1H, H_β, $J(H_\beta H_\alpha)$ = 5.5 Hz), 7.01 (d, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\alpha'})$ = 5.5 Hz), 3.60 (s, 3H, OMe), 2.53 (s, 3H, Me), 2.48 (s, 3H, Me). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −115.5 (d, $2F_o$, $J(F_oF_m)$ = 22.9 Hz), −161.2 (t, $1F_p$, $J(F_mF_p)$ = 21.2 Hz), −163.2 (m, $2F_m$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ($SiMe_4$) 151.6−122.4 (Me_2*bipy*), 50.9 (CO_2*Me*), 21.6 (*Me*$_2$bipy).

Data for Complex 7. Yield: 37 mg, 55%. Anal. Calcd for $C_{20}H_{11}N_2F_5O_2Pd$: C, 46.9; H, 2.2; N, 5.5. Found: C, 46.8; H, 2.3; N, 5.3. Mp: 190 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1640; ν(Pd−C_6F_5), 780. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 9.18 (dd, 1H, H_α, $J(H_\alpha H_\beta)$ = 4.9 Hz, $J(H_\alpha H_\gamma)$ = 1.3 Hz), 8.48 (dd, 1H, H_γ, $J(H_\beta H_\gamma)$ = 8.2 Hz, $J(H_\alpha H_\gamma)$ = 1.3 Hz), 8.39 (dd, 1H, $H_{\gamma'}$, $J(H_{\beta'}H_{\gamma'})$ = 8.2 Hz, $J(H_{\alpha'}H_{\gamma'})$ = 1.3 Hz), 8.16 (dd, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'})$ = 4.9 Hz, $J(H_{\alpha'}H_{\gamma'})$ = 1.3 Hz), 7.91 (s, 1H, H_δ or $H_{\delta'}$), 7.90 (s, 1H, H_δ or $H_{\delta'}$), 7.80 (dd, 1H, H_β, $J(H_\beta H_\gamma)$ = 8.2 Hz, $J(H_\alpha H_\beta)$ = 4.9 Hz), 7.64 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'})$ = 8.2 Hz, $J(H_{\alpha'}H_{\beta'})$ = 4.9 Hz), 3.60 (s, 3H, Me). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −115.2 (d, $2F_o$, $J(F_oF_m)$ = 22.9 Hz), −161.0 (t, $1F_p$, $J(F_mF_p)$ = 20.0 Hz), −163.2 (m, $2F_m$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ($SiMe_4$) 152.5−125.2 (phen), 20.0 (CO_2*Me*).

Data for Complex 8. Yield: 47 mg, 80%. Anal. Calcd for $C_{14}H_{19}N_2F_5O_2Pd$: C, 37.5; H, 4.3; N, 6.2. Found: C, 37.3; H, 4.4; N, 6.0. Mp: 140 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1650; ν(Pd−C_6F_5), 780. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 3.40 (s, 3H, OMe), 2.71 (s, 6H, Me), 2.65 (m, 2H, CH_2), 2.54 (m, 2H, CH_2), 2.27 (s, 6H, Me). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −116.6 (d, $2F_o$, $J(F_oF_m)$ = 22.9 Hz;), −161.5 (t, $1F_p$, $J(F_mF_p)$ = 19.8 Hz), −163.7 (m, $2F_m$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ($SiMe_4$) 183.6 (*C*O$_2$Me), 60.7−59.6 (CH_2 of tmeda), 50.5 (CO_2*Me*), 49.8−48.6 (CH_3 of tmeda).

Reaction of [(bipy)Pd(CO)(C_6F_5)]ClO_4 with NaOMe. To a solution of [(bipy)Pd(CO)(C_6F_5)]ClO_4 (80 mg, 0.152 mmol) in methanol (15 mL) was added NaOMe (16.5 mg, 0.304 mmol). The resulting solution was stirred for 1.5 h and then concentrated under vacuum until precipitation of complex **5**, which was collected by filtration and air-dried. Yield: 60%.

Preparation of Complexes [(N−N)Pd(C_6F_5)(COOR)] [N−N = Bis(3,5-dimethylpyrazol-1-yl)methane, $CH_2(C_3HMe_2N_2)_2$; R = Me (9), Et (10), or ^{i}Pr (11)]. To a suspension of [(N−N)Pd-(C_6F_5)Cl] (100 mg, 0.19 mmol) in the corresponding alcohol ROH (R = Me, Et, or ^{i}Pr) (15 mL) was added KOH(aq) (11 mg, 0.19 mmol). The suspension was stirred for 15 min, and a CO stream was then passed through the resulting mixture for 5 min. Stirring was continued for 30 min, and the mixture was then filtered through Celite to remove some KCl and traces of palladium metal. The filtrate was concentrated under vacuum. The addition of water caused the precipitation of a white solid which was collected by filtration, washed with water, and air-dried.

Data for Complex 9. Yield: 70 mg, 65%. Anal. Calcd for $C_{19}H_{19}N_4F_5O_2Pd$: C, 42.5; H, 3.5; N, 10.4. Found: C, 42.2; H, 3.6; N, 10.1. Mp: 146 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1640; ν(Pd−C_6F_5), 790. ^{1}H NMR ($CDCl_3$, ambient temperature): δ($SiMe_4$) 7.20 (br, 1H, CH_2), 6.10 (br, 1H, CH_2), 5.91 (s, 1H, H4′), 5.77 (s, 1H, H4), 3.52 (s, 3H, CO_2Me), 2.39 (s, 3H, Me3′), 2.35 (s, 3H, Me5), 2.30 (s, 3H, Me5′), 1.68 (s, 3H, Me3). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −116.3 (br, $2F_o$), −162.3 (t, $1F_p$, $J(F_mF_p)$ = 20.3 Hz), −164.7 (m, $2F_m$).

Data for Complex 10. Yield: 82 mg, 78%. Anal. Calcd for $C_{20}H_{21}N_4F_5O_2Pd$: C, 43.6; H, 3.8; N, 10.2. Found: C, 43.4; H, 3.6; N, 9.9.

Mp: 157 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1632; ν(Pd−C_6F_5), 790. ^{1}H NMR ($CDCl_3$, ambient temperature): δ($SiMe_4$) 7.05 (br, 1H, CH_2), 5.90 (br, 1 H, CH_2), 5.85 (s, 1H, H4′), 5.70 (s, 1H, H4), 3.9 (br, 2H, CH_2 of CO_2Et), 2.32 (s, 3H, Me3′), 2.29 (s, 3H, Me5), 2.26 (s, 3H, Me5′), 1.79 (s, 3H, Me3), 1.02 (t, 3H, CH_3 of CO_2Et, J(HH) = 7.1 Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −116.2 (br, $2F_o$), −162.5 (t, $1F_p$, $J(F_mF_p)$ = 20.3 Hz), −165.0 (m, $2F_m$).

Data for Complex 11. Yield: 60 mg, 56%. Anal. Calcd for $C_{21}H_{23}ClN_4F_5O_2Pd$: C, 44.6; H, 4.0; N, 9.9. Found: C, 44.3; H, 3.8; N, 10.1. Mp: 174 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1638; ν(Pd−C_6F_5), 792. ^{1}H NMR ($CDCl_3$, ambient temperature): δ($SiMe_4$) 7.1 (br, 1H, CH_2), 5.9 (br, 1H, CH_2), 5.85 (s, 1H, H4′), 5.69 (s, 1H, H4), 5.01 (sept, 1H, *CH*$(CH_3)_2$, J(HH) = 6.3 Hz), 2.32 (s, 3H, Me3′), 2.29 (s, 6H, Me5 and Me5′), 1.79 (s, 3H, Me3), 1.0 (br, 6H, CH(*CH*$_3$)$_2$). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −115.8 (br, $2F_o$), −162.6 (t, $1F_p$, $J(F_mF_p)$ = 20.3 Hz), −165.2 (br, $2F_m$).

Preparation of Complexes [(N−N)(C_6F_5)Pd(μ-CO_3)Pd(C_6F_5)-(N−N)] [N−N = bipy (12) or Me_2bipy (13)]. CO_2 was bubbled through a suspension containing the hydroxo complex **1** (60 mg, 0.134 mmol) in tetrahydrofuran (15 mL) for 5 min. After partial evaporation of the solvent, the pale yellow precipitate of **12** was filtered off and air-dried. The experimental procedure for **13** was similar but using the hydroxo complex **2** (60 mg, 0.126 mmol) and dichloromethane (5 mL).

Data for Complex 12. Yield: 51 mg, 83%. Anal. Calcd for $C_{33}H_{16}N_4F_{10}O_3Pd_2$: C, 43.1; H, 1.8; N, 6.1. Found: C, 43.2; H, 1.9; N, 6.0. Mp: 199 °C. IR (Nujol, cm^{-1}): ν_{asym}(OCO of CO_3), 1540; ν_{sym}(OCO of CO_3), 1300; ν(Pd−C_6F_5), 785. ^{1}H NMR (($CD_3)_2$SO): δ($SiMe_4$) 8.60 (d, 4H, $H_\alpha + H_{\alpha'}$, $J(H_\alpha H_\beta) \cong J(H_{\alpha'}H_{\beta'}) \cong$ 7 Hz), 8.33−8.25 (m, 6H, $H_\gamma + H_{\gamma'} + H_\delta$), 7.90 (d, 2H, $H_{\delta'}$, $J(H_{\gamma'}H_{\delta'})$ = 4.6 Hz), 7.61 (dd, 2H, H_β, $J(H_\alpha H_\beta \cong J(H_\beta H_\gamma) \cong$ 7 Hz), 7.50 (dd, 2H, $H_{\beta'}$, $J(H_{\alpha'}H_{\beta'}) \cong J(H_{\beta'}H_{\gamma'}) \cong$ 7 Hz); ^{19}F NMR: δ($CFCl_3$) −116.9 (d, $4F_o$, $J(F_oF_m)$ = 24.6 Hz), −161.3 (t, $2F_p$, $J(F_mF_p)$ = 19.8 Hz), −163.3 (m, $4F_m$).

Data for Complex 13. Yield: 47 mg, 76%. Anal. Calcd for $C_{35}H_{20}N_4F_{10}O_3Pd_2$: C, 45.56; H, 2.48; N, 5.74. Found: C, 45.38; H, 2.51; N, 5.75. Mp: 226°C dec. IR (Nujol, cm^{-1}): ν_{asym}(OCO of CO_3), 1548; ν_{sym}(OCO of CO_3), 1300; ν(Pd−C_6F_5), 790. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.88 (d, 2H, H_α, $J(H_\alpha H_\beta)$ = 5.4 Hz), 7.82 (s, 4H, $H_\delta + H_{\delta'}$), 7.80(d, 2H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'})$ = 5.5 Hz), 7.46 (d, 2H, H_β, $J(H_\alpha H_\beta)$ = 5.4 Hz), 7.11 (d, 2H, $H_{\beta'}$, $J(H_{\alpha'}H_{\beta'})$ = 5.4 Hz), 2.58 (s, 6H, Me), 2.50 (s, 6H, Me′). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.0 (m, $4F_o$), −159.6 (t, $2F_p$, $J(F_mF_p)$ = 20.7 Hz), −162.6 (m, $4F_m$).

Preparation of Complexes [(N−N)Pd(C_6F_5){SC(OR)NPh}] [N−N = bipy, R = Me (14), Et (15), or Pr (16); N−N = Me_2bipy, R = Me (17), Et (18), or Pr (19); N−N = phen, R = Me (20), Et (21), or Pr (22); N−N = tmeda, R = Me (23), Et (24), or Pr (25)]. To a solution of the corresponding hydroxo-

palladium complex [(N−N)Pd(OH)(C_6F_5)] (0.134 mmol) in alcohol (MeOH, EtOH, or PrOH) (10 mL) was added PhNCS (0.134 mmol). The resulting solution was stirred at room temperature for 1 h, and then solvent was partially eliminated under reduced pressure to give a yellow suspension. The solid was collected by filtration and air-dried.

Data for Complex 14. Yield: 54 mg, 68%. Anal. Calcd for $C_{24}H_{16}N_3F_5OPdS$: C, 48.4; H, 2.7; N, 7.1; S, 5.4. Found: C, 48.0; H, 2.5; N, 6.9; S, 5. Mp: 209 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1600, 1580; ν(Pd−C_6F_5), 790. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 9.03 (d, 1H, H_α, $J(H_\alpha H_\beta) = 5.0$ Hz), 8.01 (m, 4H, $H_\gamma + H_{\gamma'} + H_\delta + H_{\delta'}$), 7.89 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.50 (dd, 1H, H_β, $J(H_\beta H_\gamma) = 8.2$ Hz, $J(H_\alpha H_\beta) = 5.0$ Hz), 7.36 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz, $J(H_{\alpha'}H_{\beta'}) = 5.9$ Hz), 7.14 (d, 2H, H_o of NPh, $J = 7.7$ Hz), 6.80 (m, 3H, $H_p + H_m$ of NPh), 3.60 (s, 3H, OCH_3). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.3 (d, 2F_o, $J(F_oF_m) = 22.8$ Hz), −160.3 (t, 1F_p, $J(F_mF_p) = 20.0$ Hz), −163.4 (m, 2F_m).

Data for Complex 15. Yield: 51 mg, 63%. Anal. Calcd for $C_{25}H_{18}N_3F_5OPdS$: C, 49.2; H, 3.0; N, 6.9; S, 5.3. Found: C, 48.9; H, 3.0; N, 6.6; S, 5.1. Mp: 181 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1600, 1584; ν(Pd−C_6F_5), 790. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 9.02 (d, 1H, H_α, $J(H_\alpha H_\beta) = 5.2$ Hz), 8.00 (m, 4H, $H_\gamma + H_{\gamma'} + H_\delta + H_{\delta'}$), 7.88 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.46 (dd, 1H, H_β, $J(H_\gamma H_\beta) = 8.2$, $J(H_\alpha H_\beta) = 5.2$ Hz), 7.35 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.10 (d, 2H, H_o of NPh, $J = 7.9$ Hz), 6.81 (m, 3H, $H_p + H_m$ of NPh), 4.06 (q, 2H, O$CH_2$$CH_3$, $J = 7.1$ Hz), 1.10 (t, 3H, OCH_2CH_3, $J = 7.1$ Hz). ^{19}F NMR ($CDCl_3$): δ-($CFCl_3$) −116.9 (d, 2F, F_o, $J(F_oF_m) = 21.4$ Hz), −160.4 (t, 1F, F_p, $J(F_mF_p) = 20.0$ Hz), −163.3 (m, 2F, F_m).

Data for Complex 16. Yield: 58 mg, 69%. Anal. Calcd for $C_{26}H_{20}N_3F_5OPdS$: C, 50.1; H, 3.2; N, 6.7; S, 5.1. Found: C, 50.2; H, 3.2; N, 6.5; S, 5.0. Mp: 169°C dec. IR (Nujol, cm^{-1}): ν(C═N), 1600, 1588; ν(Pd−C_6F_5), 788. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 9.06 (d, 1H, H_α, $J(H_\alpha H_\beta) = 5.2$ Hz), 7.97 (m, 4H, $H_\gamma + H_{\gamma'} + H_\delta + H_{\delta'}$), 7.86 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.2$ Hz), 7.46 (dd, 1H, H_β, $J(H_\beta H_\gamma) = 8.2$ Hz, $J(H_\alpha H_\beta) = 5.2$ Hz), 7.34 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz, $J(H_{\alpha'}H_{\beta'}) = 5.2$ Hz), 7.16 (d, 2H, H_o of NPh, $J(H_{\beta'}H_{\gamma'}) = 7.9$ Hz), 6.82 (m, 3H, $H_p + H_m$ of NPh), 3.95 (t, 2H, OCH_2-CH_2CH_3, $J = 6.8$ Hz), 1.43 (m, 2H, $OCH_2CH_2CH_3$, $J = 7.1$ Hz), 0.67 (t, 3H, $OCH_2CH_2CH_3$, $J = 7.3$ Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −1172 (d, 2F_o, $J(F_oF_m) = 23.1$ Hz), −160.5 (t, 1F_p, $J(F_mF_p) = 19.8$ Hz), −163.2 (m, 2F_m).

Data for Complex 17. Yield: 46 mg, 55%. Anal. Calcd for $C_{26}H_{20}N_3F_5OPdS$: C, 50.1; H, 3.2; N, 6.7; S, 5.1. Found: C, 49.9; H, 3.0; N, 6.6; S, 5.0. Mp: 204 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1608, 1588; ν(Pd−C_6F_5), 788. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.80 (d, 1H, H_α, $J(H_\alpha H_\beta) = 5.4$ Hz), 7.80 (s, 1H, H_δ or $H_{\delta'}$), 7.76 (s, 1H, H_δ or $H_{\delta'}$), 7.65 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.4$ Hz), 7.24 (d, 1H, H_β, $J(H_\alpha H_\beta) = 5.4$ Hz), 7.14 (d, 2H, H_o of NPh, $J = 8.0$ Hz), 7.07 (d, 1H, $H_{\beta'}$, $J(H_{\alpha'}H_{\beta'}) = 5.4$ Hz), 6.86 (t, 1H, H_p of NPh, $J = 8.0$ Hz), 6.76 (m, 2H, H_m of NPh), 3.58 (s, 3H, OCH_3), 2.45 (s, 3H, Me_2bipy), 2.42 (s, 3H, Me_2bipy). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.2 (d, 2F_o, $J(F_oF_m) = 19.8$ Hz), −160.5 (t, F_p, $J(F_mF_p) = 19.8$ Hz), −163.5 (m, 2F_m).

Data for Complex 18. Yield: 58 mg, 68%. Anal. Calcd for $C_{27}H_{22}N_3F_5OPdS$: C, 50.8; H, 3.5; N, 6.6; S, 5.0. Found: C, 50.3; H, 3.5; N, 6.4; S, 5.1. Mp: 206 °C. IR (Nujol, cm^{-1}): ν(C═N), 1580; ν(Pd−C_6F_5), 795. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.78 (d, 1H, H_α, $J(H_\alpha H_\beta) = 5.4$ Hz), 7.81 (s, 1H, H_δ or $H_{\delta'}$), 7.76 (s, 1H, H_δ or $H_{\delta'}$), 7.64 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.5$ Hz), 7.20 (m, 4H, $H_\beta + H_{\beta'}$ of Me_2bipy + H_o of NPh), 6.81 (m, 3H, $H_p + H_m$ of NPh), 2.46 (s, 3H, Me_2bipy), 2.43 (s, 3H, Me_2bipy), 4.01 (q, 2H, O$CH_2$$CH_3$, $J =$ 7.0 Hz), 1.08 (t, 3H, OCH_2CH_3, $J = 7.0$ Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −119.7 (d, 2F_o, $J(F_oF_m) = 22.8$ Hz), −160.7 (t, 1F_p, $J(F_mF_p) = 19.8$ Hz), −163.5 (m, 2F_m).

Data for Complex 19. Yield: 56 mg, 64%. Anal. Calcd for $C_{28}H_{24}N_3F_5OPd$: C, 51.6; H, 3.7; N, 6.4; S, 4.9. Found: C, 51.3; H, 3.5; N, 6.6; S, 5.1. Mp: 204 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1580; ν(Pd−C_6F_5), 795. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.86 (d, 1H, H_α, $J(H_\alpha H_\beta) = 5.4$ Hz), 7.81 (s, 1H, H_δ or $H_{\delta'}$), 7.77 (s, 1H, H_δ or $H_{\delta'}$), 7.65 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.5$ Hz), 7.27 (d, 1H, H_β, $J(H_\alpha H_\beta) = 5.4$ Hz), 7.15 (m, 3H, $H_{\beta'}$ of Me_2bipy + H_o of NPh), 6.82 (m, 3H, $H_p + H_m$ of NPh), 3.94 (t, 2H, O$CH_2$$CH_2CH_3$, $J = 6.8$ Hz), 2.45 (s, 3H, Me_2bipy), 2.42 (s, 3H, Me_2bipy), 1.43 (m, 2H, $OCH_2CH_2CH_3$), 0.68 (t, 3H, $OCH_2CH_2CH_3$, $J = 7.3$ Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.1 (d, 2F_o, $J(F_oF_m) = 22.8$ Hz), −160.8 (t, 1F_p, $J(F_mF_p) = 19.8$ Hz), −163.5 (m, 2F_m).

Data for Complex 20. Yield: 53 mg, 64%. Anal. Calcd for $C_{26}H_{16}N_3F_5OPdS$: C, 50.4; H, 2.6; N, 6.8; S, 5.2. Found: C, 50.2; H, 2.8; N, 6.6; S, 5.1. Mp: 217 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1572; ν(Pd−C_6F_5), 799. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 9.29 (dd, 1H, H_α, $J(H_\alpha H_\beta) = 5.0$ Hz, $J(H_\alpha H_\gamma) = 1.3$ Hz), 8.46 (d, 2H, $H_\gamma + H_{\gamma'}$, $J(H_\beta H_\gamma) = J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz), 8.20 (dd, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz, $J(H_{\alpha'}H_{\gamma'}) = 1.3$ Hz), 7.92 (m, 2H, $H_\delta + H_{\delta'}$), 7.80 (dd, 1H, H_β, $J(H_\beta H_\gamma) = 8.2$ Hz, $J(H_\alpha H_\beta) = 5.0$ Hz), 6.92 (dd, 1H, $H_{\beta'}$, 1H, $J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.12 (m, 2H, H_o of NPh), 6.84 (m, 3H, $H_p + H_m$ of NPh), 3.62 (s, 3H, OCH_3). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.2 (d, 2F_o, $J(F_oF_m) = 21.5$ Hz), −160.2 (t, 1F_p, $J(F_mF_p) = 19.8$ Hz), −163.4 (m, 2F_m).

Data for Complex 21. Yield: 54 mg, 64%. Anal. Calcd for $C_{27}H_{18}N_3F_5OPdS$: C, 51.2; H, 2.9; N, 6.6; S, 5.1. Found: C, 51.1; H, 2.9; N, 6.4; S, 5.1. Mp: 209 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1574; ν(Pd−C_6F_5), 796. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 9.18 (dd, 1H, H_α, $J(H_\alpha H_\beta) = 5.0$ Hz, $J(H_\alpha H_\gamma) = 1.3$ Hz), 8.44 (d, 2H, $H_\gamma + H_{\gamma'}$, $J = 8.1$ Hz), 8.17 (dd, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz, $J(H_{\alpha'}H_{\gamma'}) = 1.3$ Hz), 7.90 (m, 2H, $H_\delta + H_{\delta'}$), 7.80 (dd, 1H, H_β, $J(H_\beta H_\gamma) = 8.2$ Hz, $J(H_\alpha H_\beta) = 5.0$ Hz), 6.92 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.12 (m, 2H, H_o of NPh), 6.84 (m, 3H, $H_p + H_m$ of NPh), 4.07 (q, 2H, O$CH_2$$CH_3$, $J = 7.0$ Hz), 1.07 (t, 3H, OCH_2CH_3, $J = 7.0$ Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −116.7 (d, 2F_o, $J(F_oF_m) = 22.8$ Hz), −160.4 (t, 1F_p, $J(F_oF_m) = 19.8$ Hz), −163.3 (m, 2F_m).

Data for Complex 22. Yield: 51 mg, 59%. Anal. Calcd for $C_{28}H_{20}N_3F_5OPdS$: C, 51.9; H, 3.1; N, 6.5; S, 5.0. Found: C, 51.8; H, 2.9; N, 6.2; S, 4.7. Mp: 204 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1574; ν(Pd−C_6F_5), 796. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 9.22 (d, 1H, H_α, $J(H_\alpha H_\beta) = 5.0$ Hz), 8.44 (d, 2H, $H_\gamma + H_{\gamma'}$, $J(H_\beta H_\gamma) = J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz), 8.16 (d, 1H, $H_{\alpha'}$, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.92 (d, 1H, H_δ or $H_{\delta'}$, $J(H_\delta H_{\delta'}) = 8.1$ Hz), 7.88 (d, 1H, H_δ or $H_{\delta'}$, $J(H_\delta H_{\delta'}) = 8.1$ Hz), 7.75 (dd, 1H, H_β, $J(H_\beta H_\gamma) = 8.2$ Hz, $J(H_\alpha H_\beta) = 5.0$ Hz), 7.63 (dd, 1H, $H_{\beta'}$, $J(H_{\beta'}H_{\gamma'}) = 8.2$ Hz, $J(H_{\alpha'}H_{\beta'}) = 5.0$ Hz), 7.12 (m, 2H, H_m of NPh), 6.90 (d, 2H, H_o of NPh, $J = 7.2$ Hz), 6.84 (t, 1H, H_p of NPh, $J = 7.2$ Hz), 3.96 (t, 2H, OCH_2 CH_2CH_3, $J = 7.0$ Hz), 1.43 (m, 2H, $OCH_2CH_2CH_3$), 0.60 (t, 3H, $OCH_2CH_2CH_3$, J = 7.3 Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −116.9 (d, 2F_o, $J(F_oF_m)$ = 19.1 Hz), −160.5 (t, 1F_p, $J(F_mF_p) = 21.0$ Hz), −163.2 (m, 2F_m).

Data for Complex 23. Yield: 51 mg, 69%. Anal. Calcd for $C_{20}H_{24}N_3F_5OPdS$: C, 43.2; H, 4.4; N, 7.6; S, 5.8. Found: C, 43.0; H, 4.2; N, 7.4; S, 5.6. Mp: 155 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1602, 1588; ν(Pd−C_6F_5), 786. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 7.13 (m, 2H, H_m of NPh), 6.86 (t, 1H, H_p of NPh, $J = 7.5$ Hz), 6.60 (d, 2H, H_o of NPh, $J = 7.6$ Hz), 3.64 (s, 3H, OCH_3), 2.61 (m, 4H, CH_2 of tmeda), 2.55 (s, 3H, CH_3 of tmeda), 2.44 (s, 3H, CH_3 of tmeda). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −118.7 (d, 2F_o, $J(F_oF_m) =$ 22.8 Hz), −161.2 (t, 1F_p, $J(F_mF_p) = 19.8$ Hz), −164.1 (m, 2F_m).

Table 1. Crystal Data and Structure Refinement for **8**, **13**·$2CH_2Cl_2$, and **23**

	8	**13**·$2CH_2Cl_2$	**23**
empirical formula	$C_{14}H_{19}F_5N_2O_2Pd$	$C_{37}H_{24}F_{10}N_4O_3Pd_2{\cdot}2CH_2Cl_2$	$C_{20}H_{24}F_5N_3OPdS$
M_T	448.7	1145.25	555.88
T (K)	293	173	293
λ (Å)	0.71073	0.71073	0.71073
space group	$P2(1)/c$	P-**1**	$P2(1)/n$
a (Å)	11.792(2)	11.1311(6)	11.297(2)
b (Å)	13.370(3)	11.6741(7)	12.697(2)
c (Å)	11.498(2)	17.0116(8)	16.825(3)
α (deg)	90	70.810(4)	90
β (deg)	96.37(2)	84.557(4)	108.791(15)
γ (deg)	90	84.114(4)	90
V (Å^3)	1801.5(6)	2072.34(19)	2284.7(8)
Z	4	2	4
ρ (Mg m^{-3})	1.65	1.835	1.616
μ (mm^{-1})	1.07	1.215	0.960
θ range (deg)	2−25	3−25	2−25
index ranges	$-14 \le h \le \mp 14$	$-13 \le h \le \mp 5$	$0 \le h \le 13$
	$0 \le k \le 15$	$-13 \le k \le \mp 13$	$0 \le k \le 15$
	$0 \le l \le 13$	$-20 \le l \le \mp 20$	$-19 \le l \le \mp 18$
no. of reflns collected	3469	10850	4216
absorption correction	ψ scans	none	ψ scans
no. of data/restraints/params	3311/0/217	7209/1/564	4008/0/280
GOF on F^2	1.5	0.869	1.059
final R indices [$I > 2\sigma(I)$]	R1 = 0.047	R1 = 0.032	R1 = 0.033
		wR2 = 0.083	wR2 = 0.080
R indices (all data)	R1 = 0.054	R1 = 0.043	R1 = 0.043
		wR2 = 0.087	wR2 = 0.085

Data for Complex 24. Yield: 52 mg, 68%. Anal. Calcd for $C_{21}H_{26}N_3F_5OPdS$: C, 44.3; H, 4.6; N, 7.4; S, 5.6. Found: C, 44.0; H, 4.7; N, 7.6; S, 5.9. Mp: 157 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1598, 1586; ν(Pd−C_6F_5), 786. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 7.15 (m, 2H, H_m of NPh), 6.85 (t, 1H, H_p of NPh, J = 7.3 Hz), 6.61 (d, 2H, H_o of NPh, J = 7.5 Hz), 4.11 (q, 2H, OCH_2CH$_3$, J = 7.1 Hz), 2.66 (s, 4H, CH_2 of tmeda), 2.60 (s, 3H, CH_3 of tmeda), 2.56 (s, 3H, CH_3 of tmeda), 1.33 (t, 3H, OCH$_2$$CH_3$, J = 7.1 Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −118.7 (d, 2F$_o$, J(F$_o$F$_m$) = 22.8 Hz), −161.2 (t, 1F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −164.1 (m, 2F$_m$).

Data for Complex 25. Yield: 53 mg, 68%. Anal. Calcd for $C_{22}H_{28}N_3F_5OPdS$: C, 45.3; H, 4.8; N, 7.2; S, 5.5. Found: C, 45.0; H, 4.7; N, 7.5; S, 5.7. Mp: 151 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1604, 1590; ν(Pd−C_6F_5), 786. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 7.16 (m, 2H, H_m of NPh), 6.66 (t, 1H, H_p of NPh, J = 7.5 Hz), 6.60 (d, 2H, H_o of NPh, J = 7.5 Hz), 4.09 (t, 2H, OCH_2CH$_2$CH$_3$, J = 7.2 Hz), 2.66 (s, 4H, CH_2 of tmeda), 2.62 (s, 3H, CH_3 of tmeda), 2.49 (s, 3H, CH_3 of tmeda), 1.81 (m, 2H, OCH$_2$$CH_2CH_3$), 1.08 (t, 3H, OCH$_2CH_2$$CH_3$, J = 7.2 Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −118.7 (d, 2F$_o$, J(F$_o$F$_m$) = 22.8 Hz), −161.4 (t, 1F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −164.0 (m, 2F$_m$).

Preparation of the Complex [(bipy)Pd(C_6F_5){N(Ph)C(O)OR)}] (26). To a solution of [(bipy)Pd(OH)(C_6F_5)] (50 mg, 0.111 mmol) in methanol (15 mL) was added PhNCO (0.111 mmol). The resulting solution was stirred at room temperature for 1 h to give a yellow suspension which was partially concentrated under reduced pressure. The solid was collected by filtration and air-dried.Yield: 58%. Anal. Calcd for $C_{24}H_{16}N_3F_5O_2Pd$: C, 49.7; H, 2.8; N, 7.3. Found: C, 49.5; H, 2.7; N, 7.1. Mp: 206 °C dec. IR (Nujol, cm^{-1}): ν(CO), 1644; ν(Pd−C_6F_5), 786. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.64 (d, 1H, H_α, J($H_\alpha H_\beta$) = 5.0 Hz), 8.09 (m, 4H, H_γ + $H_{\gamma'}$ + H_δ + $H_{\delta'}$), 7.94 (d, 1H, $H_{\alpha'}$, J($H_{\alpha'}H_{\beta'}$) = 5.0 Hz), 7.56 (m, 3H, H_o of NPh + H_β), 7.35 (dd, 1H, $H_{\beta'}$, J($H_{\beta'}H_{\gamma'}$) = 8.2 Hz, J($H_{\alpha'}H_{\beta'}$) = 4.9 Hz), 7.06 (m, 2H, H_m of NPh), 6.81 (t, 1H, H_p of NPh, J = 7.4 Hz), 3.66 (s, 3H, OCH_3). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −119.3 (m, 1F$_o$), −120.0 (m, 1F$_o$), −160.3 (t, 1F$_p$, J(F$_m$F$_p$) = 19.8 Hz), −162.9 (m, 1F$_m$), −163.4 (m, 1F$_m$).

Preparation of Complexes [(N−N)Pd(C_6F_5){SC(NEt_2)NPh}] [N−N = bipy (27), Me_2bipy (28), or phen (29)]. To a suspension of [(N−N)Pd(OH)(C_6F_5)] (60 mg, 0.134 mmol) in acetone (20 mL) was added diethylamine (0.160 mmol). After 5 min of stirring, PhNCS (0.134 mmol) was also added. The resulting suspension was stirred for 2 h to give a yellow solution. Then solvent was partially eliminated under reduced pressure to yield a yellow precipitate. The solid was collected by filtration and air-dried.

Data for Complex 27. Yield: 47 mg, 55%. Anal. Calcd for $C_{27}H_{23}N_4F_5PdS$: C, 50.9; H, 3.6; N, 8.8; S, 5.0. Found: C, 50.5; H, 3.7; N, 8.8; S, 4.8. Mp: 262 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1538; ν(Pd−C_6F_5), 788. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.64 (m, 1H, H_α), 8.0−7.8 (m, 5H, H_γ + $H_{\gamma'}$ + $H_{\alpha'}$ + H_δ + $H_{\delta'}$), 7.30 (m, 2H, H_β + $H_{\beta'}$), 6.89 (d, 2H, H_o of NPh, J = 7.5 Hz), 6.59 (dd, 2H, H_m of NPh, J = 7.5 Hz), 6.07 (t, 1H, H_p of NPh, J = 7.5 Hz), 3.32 (q, 4H, NCH_2, J = 7.5 Hz), 0.97 (t, 6H, NCH_2CH_3, J = 7.5 Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.1 (d, 2F$_o$, J(F$_o$F$_m$) = 23.7 Hz), −161.4 (t, 1F$_p$, J(F$_m$F$_p$) = 21.6 Hz), −163,7 (m, 2F$_m$).

Data for Complex 28. Yield: 48 mg, 54%. Anal. Calcd for $C_{29}H_{27}N_4F_5PdS$: C, 52.4; H, 4.1; N, 8.4; S, 4.8. Found: C, 52.1; H, 4.1; N, 8.4; S, 4.6. Mp: 182 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1548; ν(Pd−C_6F_5), 786. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.42 (d, 1H, H_α, J($H_\alpha H_\beta$) = 5.4 Hz), 7.74 (s, 1H, H_δ or $H_{\delta'}$), 7.63 (m, 2H, H_δ or $H_{\delta'}$ + $H_{\alpha'}$), 7.05 (d, 2H, H_β + $H_{\beta'}$, J($H_{\alpha'}H_{\beta'}$) = J($H_\alpha H_\beta$) = 5.4 Hz), 6.87 (d, 2H, H_o of NPh, J = 7.5 Hz), 6.62 (dd, 2H, H_m of NPh, J = 7.5 Hz), 6.11 (t, 1H, H_p of NPh, J = 7.5 Hz), 3.33 (q, 4H, NCH_2, J = 7.5 Hz), 2.43 (s, 6H, Me_2bipy), 0.95 (t, 6H, NCH_2CH_3, J = 7.5 Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.0 (d, 2F$_o$, J(F$_o$F$_m$) = 22.2 Hz), −161.6 (t, 1F$_p$, J(F$_m$F$_p$) = 20.4 Hz), −163.8 (m, 2F$_m$).

Data for Complex 29. Yield: 58 mg, 65%. Anal. Calcd for $C_{29}H_{23}N_4F_5PdS$: C, 52.7; H, 3.5; N, 8.5; S, 4.9. Found: C, 52.8; H, 3.0; N, 8.4; S, 4.6. Mp: 204 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1552; ν(Pd−C_6F_5), 790. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 8.80 (d, 1H, H_α, J($H_\alpha H_\beta$) = 5.0 Hz), 8.42 (d, 1H, H_γ, J($H_\beta H_\gamma$) = 8.2 Hz), 8.30 (d, 1H, $H_{\gamma'}$, J($H_{\beta'}H_{\gamma'}$) = 8.2 Hz), 8.14 (d, 1H, $H_{\alpha'}$, J($H_{\alpha'}H_{\beta'}$) = 5.0 Hz), 7.86 (m, 2H, H_δ + $H_{\delta'}$), 7.60 (m, 2H, H_β + $H_{\beta'}$), 6.90 (d, 2H,

H_o of NPh, $J = 7.5$ Hz), 6.38 (dd, 2H, H_m of NPh, $J = 7.5$ Hz), 5.82 (t, 1H, H_p of NPh, $J = 7.5$ Hz), 3.37 (q, 4H, NCH_2, $J = 7.5$ Hz), 0.98 (t, 6H, NCH_2CH_3, $J = 7.5$ Hz). ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −116.9 (d, $2F_o$, $J(F_oF_m) = 24.0$ Hz), −161.3 (t, $1F_p$, $J(F_mF_p) = 21.6$ Hz), −163.7 (m, $2F_m$).

Preparation of the Complex [(tmeda)Pd(C_6F_5){SC(NEt_2)NPh}] (30). To a solution of [(tmeda)Pd(OH)(C_6F_5)] (60 mg, 0.134 mmol) in acetone (20 mL) was added diethylamine (0.160 mmol). After 5 min of stirring, PhNCS (0.134 mmol) was also added. The resulting solution was stirred for 2 h. Then solvent was partially eliminated under reduced pressure. Addition of hexane caused the precipitation of a solid which was collected by filtration and air-dried. Yield: 68 mg, 85%. Anal. Calcd for $C_{23}H_{31}N_4F_5PdS$: C, 46.3; H, 5.2; N, 9.4; S, 5.4. Found: C, 46.0; H, 5.0; N, 9.0; S, 5.1. Mp: 110 °C dec. IR (Nujol, cm^{-1}): ν(C═N), 1556; ν(Pd−C_6F_5), 788. ^{1}H NMR ($CDCl_3$): δ($SiMe_4$) 7.13 (d, 2H, H_o of NPh, $J = 7.5$ Hz), 6.88 (dd, 2H, H_m of NPh, $J = 7.5$ Hz), 6.74 (t, 1H, H_p of NPh, $J = 7.5$ Hz), 3.25 (q, 4H, NCH_2CH_3, $J = 7.5$ Hz), 2.49 (m, 4H, CH_2 of tmeda), 2.33 (s, 6H, CH_3 of tmeda), 2.13 (s, 6H, CH_3 of tmeda), 0.89 (t, 6H, NCH_2CH_3, $J = 7.5$ Hz); ^{19}F NMR ($CDCl_3$): δ($CFCl_3$) −117.5 (d, $2F_o$, $J(F_oF_m) = 23.4$ Hz), −161.8 (t, $1F_p$, $J(F_mF_p) = 19.5$ Hz), −163.8 (m, $2F_m$).

X-ray Crystal Structure Analysis. Suitable crystals of **8**, **13**·$2CH_2Cl_2$, and **23** were grown from benzene/hexane (complexes **8** and **23**) or from dichloromethane/toluene/hexane (complex **13**). Details of the data collection and refinement are given in Table 1. The crystals were mounted onto the tip of a glass fiber, and the data collection was performed with a Enraf-Nonius CAD4 diffractometer for **8** and **23** and with a Siemens P4 diffractometer for **13**. The scan mode was $\theta-2\theta$ for **8** and **23** and $\omega-2\theta$ for **13**. The structures were solved by heavy atom methods, SHELXS-86[56] (complex **8**), and by direct methods, SHELXS-97[57] (complexes **13** and **23**). The structures were refined by full-matrix least-squares Enraf-Nonius MOLEN programs[58] (complex **8**) and SHELXL-97[57] (complexes **13** and **23**). In the three structures hydrogen atoms were included using a riding model.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compounds **8**, **13**, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(56) Program for Crystal Structure Solution: G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1986.
(57) Sheldrick, G. M. *SHELX-97. Programs for Crystal Structure Analysis*, Release 97-2; University of Göttingen: Göttingen, Germany, 1998.
(58) *MOLEN, CAD4 Software*, Version 5.0; Enraf-Nonius: Delft, The Netherlands, 1989.