The First Isolable Organopalladium Formato Complexes: Synthesis, Characterization, and X-ray Structure. Facile and Convenient Thermal Generation of Coordinatively Unsaturated Palladium(0) Species

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$[L_2Pd_2(R)_2(\mu\text{-}OH)_2]$ complexes (L = PPh_3, R = Ph, Me) react with formic acid in benzene to give the first stable organopalladium formates, $[L_2Pd_2(R)_2(\mu\text{-}HCOO)_2]$ (**1**, R = Ph; **2**, R = Me). Addition of L to **1** and **2** results in the formation of the less stable, but still isolable, [$L_2Pd(R)(HCOO)$] (**3**, R = Ph; **4**, R = Me). Complexes **1**−**4** have been characterized by elemental analysis and NMR and IR spectral data. The structure of **2** has been confirmed by X-ray analysis of its 1:1.5 benzene solvate: monoclinic, space group $P2_1/n$; a = 9.785(4) Å, b = 24.909(8) Å, c = 18.854(7) Å, β = 102.92(3)°; V = 4479(3) Å^3, Z = 4; D_{calcd} = 1.441 g/cm^3; R = 0.044, R_w = 0.066. The thermal decomposition of **1**−**4** in benzene or toluene at 30−55 °C gives CO_2, RH, and highly reactive [L_nPd] (n = 1, 2). An exchange between the σ-Me groups and phenyls of the PPh_3 ligand is observed in the course of the thermal decomposition of **2** in toluene at 55 °C. The thermolysis of **1** in the presence of PhI gives rise to $[L_2Pd_2(Ph)_2(\mu\text{-}I)_2]$ (**5**); likewise, the decomposition of **2** in the presence of MeI furnishes $[L_2Pd_2(Me)_2(\mu\text{-}I)_2]$ (**6**). However, when **1** is decomposed in the presence of MeI, both **5** and **6** are formed, with the ratio of **5** to **6** being higher at higher concentrations of MeI. A similar effect is observed when **2** is thermolyzed in the presence of PhI. This "reverse" selectivity leads to the recognition of two distinct mechanisms governing the Pd-catalyzed reductive dehalogenation of aryl halides with formate anion.

Organopalladium formato complexes have been proposed as key catalytic intermediates in a number of synthetically valuable processes, such as the preparation of terminal olefins from allylic esters and formic acid,[1,2] the reductive dehalogenation of haloarenes with formate anion,[3] and some carbonylation reactions.[4] Both the unique catalytic properties of palladium[5] and the importance of transition-metal formates in the activation of CO_2[6] provide a special challenge for the synthesis and characterization of (formato)palladium complexes. In the present paper we wish to report the preparation, isolation, full characterization (including X-ray analysis), and some properties of the first (σ-organo)palladium formates. There has been only one report[7] in the literature, describing the generation (at −30 °C) and in situ characterization of (π-allyl)palla-

Table 1. Crystallographic Data for $[(Ph_3P)_2Pd_2Me_2(\mu\text{-}HCOO)_2]\cdot 1.5C_6H_6$ ($2\cdot 1.5C_6H_6$)

formula	$C_{49}H_{47}O_4P_2Pd_2$
fw	974.62
cryst shape	cube
cryst dimens, mm	0.2 × 0.2 × 0.2
cryst syst	monoclinic
lattice params	a = 9.785(4) Å b = 24.909(8) Å c = 18.854(7) Å β = 102.92(3)°
space group	$P2_1/n$
Z	4
V, Å^3	4479(3)
d_{calc}, g/cm^3	1.441
T, K	143
radiation (λ, Å)	Mo Kα (0.709 30)
μ, mm^{-1}	0.89
R (R_w), %	4.4 (6.6)

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(1) For reviews see: (a) Tsuji, J. *Pure Appl. Chem.* **1982**, *54*, 197. (b) Tsuji, J. *Pure Appl. Chem.* **1986**, *58*, 869. (c) Tsuji, J.; Takahashi, T. *Yakugaku Zasshi* **1987**, *107*, 87. (d) Shimizu, I.; Oshima, M.; Nagasawa, K.; Tsuji, J.; Mandai, T. *Yuki Gosi Kagaku Kyokaishi* **1991**, *49*, 526; *Chem. Abstr.* **1991**, *115*, 70866d.

(2) For the most recent references see: (a) Hayashi, T.; Iwamura, H.; Uozumi, Y. *Tetrahedron Lett.* **1994**, *35*, 4813. (b) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775. (c) Mandai, T.; Matsumoto, T.; Kawada, M.; Tsuji, J. *Tetrahedron* **1993**, *49*, 5483. (d) Mandai, T.; Matsumoto, T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1993**, *34*, 2161.

(3) (a) Cortese, N. A.; Heck, R. F. *J. Org. Chem.* **1977**, *42*, 3491. (b) Helquist, P. *Tetrahedron Lett.* **1978**, 1913. (c) Pri-Bar, I.; Buchman, O. *J. Org. Chem.* **1986**, *51*, 734. (d) Anwer, M. K.; Sherman, D. B.; Roney, J. G.; Spatola, A. F. *J. Org. Chem.* **1989**, *54*, 1284. (e) Ben-David, Y.; Gozin, M.; Portnoy, M.; Milstein, D. *J. Mol. Catal.* **1992**, *73*, 173.

(4) (a) Pri-Bar, I.; Buchman, O. *J. Org. Chem.* **1988**, *53*, 624. (b) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1816. (c) El Ali, B.; Alper, H. *J. Mol. Catal.* **1992**, *77*, 7. (d) El Ali, B.; Alper, H. *J. Org. Chem.* **1993**, *58*, 3595. (e) Zargarian, D.; Alper, H. *Organometallics* **1993**, *12*, 712.

(5) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer: Heidelberg, Germany, 1980. (b) Heck, R. F. *Palladium Reagents in Organic synthesis*; Academic Press: New York, 1985.

(6) (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, Germany, 1988. (b) For the most recent references see: Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231. Leitner, W.; Dinjus, E.; Gassner, F. *J. Organomet. Chem.* **1994**, *475*, 257. Gassner, F.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1465. Graf, E.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1992**, 623.

(7) Oshima, M.; Shimizu, I.; Yamamoto, A.; Ozawa, F. *Organometallics* **1991**, *10*, 1221.

(8) (a) Darnesbourg and co-workers[8b] reported the preparation of $[(Cy_3P)_2Pd(H)(HCOO)]$ for kinetic studies. The complex was characterized by ^{1}H NMR spectroscopy; however, elemental analysis was not performed, probably due to the instability of the compound. (b) Darensbourg, D. J.; Wiegreffe, P.; Riordan, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 5759.

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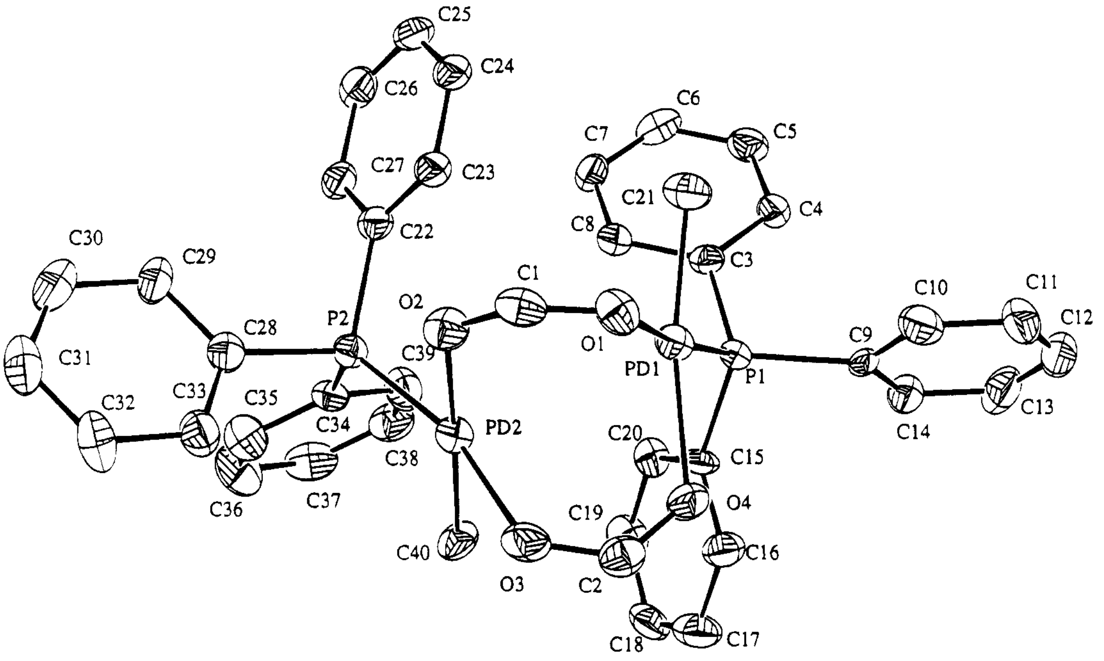

Figure 1. ORTEP drawing for the metal complex part of $2{\cdot}1.5C_6H_6$ (hydrogen atoms are omitted). Selected bond lengths (Å) and angles (deg): Pd(1)−P(1), 2.2144(21); Pd(1)−O(1), 2.124(5); Pd(1)−O(4), 2.151(5); Pd(1)−C(21), 2.036(8); Pd(2)−P(2), 2.2266(21); Pd(2)−O(2), 2.183(5); Pd(2)−O(3), 2.117(5); Pd(2)−C(40), 2.027(8); O(1)−C(1), 1.251(10); O(2)−C(1), 1.239(10); O(3)−C(2), 1.256(10); O(4)−C(2), 1.238(10); P(1)−Pd(1)−O(1), 173.58(15); P(1)−Pd(1)−O(4), 98.06(16); P(1)−Pd(1)−C(21), 87.61(24); O(1)−Pd(1)−C(21), 86.4(3); P(2)−Pd(2)−O(2), 96.07(15); P(2)−Pd(2)−O(3), 165.66(16); P(2)−Pd(2)−C(40), 89.12(24); O(2)−Pd(2)−O(3), 85.99(21); O(2)−Pd(2)−C(40), 171.9(3); O(3)−Pd(2)−C(40), 87.5(3); Pd(1)−O(1)−C(1), 125.0(5); Pd(2)−O(2)−C(1), 124.7(5); Pd(2)−O(3)−C(2), 123.8(5); Pd(1)−O(4)−C(2), 126.3(5); O(1)−C(1)−O(2), 129.1(7); O(3)−C(2)−O(4), 128.3(7).

dium formates in solution by low-temperature NMR spectroscopy.[8] These complexes, however, cannot be isolated, as they decompose rapidly at ambient temperature.[7]

Treatment of $[(Ph_3P)_2Pd_2(R)_2(\mu\text{-}OH)_2]$, where R = Ph[9] or Me (see Experimental Section), with a 1.5−7-fold excess of formic acid in benzene results in direct and clean formation of the corresponding *binuclear* organopalladium complexes with two bridging η^2-formato ligands, **1** and **2**. Both **1** and **2** readily add triphenylphosphine to give the corresponding *mononuclear* organopalladium η^1-formates, **3** and **4** (eq 1).

$$[L_2Pd_2R_2(\mu\text{-}OH)_2] \xrightarrow[-2H_2O]{2HCOOH} \underset{\mathbf{1,2}}{[L_2Pd_2R_2(\mu\text{-}HCOO)_2]} \xrightarrow{2L} \underset{\mathbf{3,4}}{2[L_2Pd(R)(HCOO)]} \quad (1)$$

$$L = PPh_3;\ R = Ph\ (\mathbf{1}, \mathbf{3}),\ Me\ (\mathbf{2}, \mathbf{4})$$

Complexes **1**−**4** were isolated in high yields (85−98%) and characterized by elemental analysis and IR and NMR spectroscopy. The structure of **2** was confirmed by a single-crystal diffraction study of its benzene solvate (Table 1). As shown in Figure 1, the two Pd atoms in **2** are held in one molecule by two bridging η^2-formato ligands cis to each other, as previously found for the closely related Pd benzoato dimer $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}PhCOO)_2]$.[10]

The binuclear complexes **1** and **2** are considerably more stable than the mononuclear **3** and **4**. In the solid state, both **1** and **2** do not decompose at room temperature for several days, whereas crystalline **3** decomposes slowly at 20 °C and solid **4** is even less stable. However, all the formato complexes **1**−**4** can be stored at −15 °C for a few weeks without any sign of decomposition. In benzene or toluene solution, mononuclear **3** and **4** start decomposing above 15 °C, to give CO_2, Pd metal, tris(triphenylphosphine)palladium(0), and benzene or methane, respectively. This reaction likely occurs via CO_2 loss, followed by reductive elimination of the corresponding hydrocarbon, RH, and disproportionation of the thus generated $[(Ph_3P)_2Pd]$ (eq 2). It is noteworthy that benzoato[10] and acetato (see Experimental Section) analogues of **1**−**4** are stable at up to 70−90 °C in benzene and toluene solutions under N_2, showing no sign of decomposition for at least 10−15 min.

$$[L_2Pd(R)(HCOO)] \xrightarrow[-CO_2]{\Delta} [L_2Pd(R)(H)] \xrightarrow[-RH]{} [L_2Pd] \rightarrow [L_3Pd] + Pd \quad (2)$$

Unlike *trans*-alkyl- or *trans*-arylbis(phosphine)platinum hydrides,[11a] their Pd analogues are too unstable for isolation or even spectral characterization in situ, decomposing immediately upon generation (eq 2).[11b] The resulting bis(triphenylphosphine)palladium[12] was not observed by ^{31}P NMR spectroscopy due to its facile disproportionation to $[(Ph_3P)_3Pd]$ under the reaction conditions. Similarly, $[(Ph_3P)_2Pt]$, generated by various means, readily transforms to $[(Ph_3P)_3Pt]$.[13] However, the in situ generation of $[(Ph_3P)_2Pd]$ was confirmed by

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[9] Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890.

[10] Grushin, V. V.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4305.

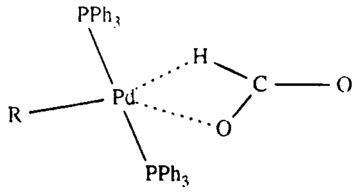
[11] (a) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, C17. (b) Two complexes, *trans*-$[L_2Pd(H)Me]$, where L = Cy_3P or i-Pr_3P, are relatively stable due to the bulky electron-rich phosphine ligands. See: Abis, L.; Santi, R.; Halpern, J. *J. Organomet. Chem.* **1981**, *215*, 263.

[12] Urata, H.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *J. Organomet. Chem.* **1989**, *364*, 235.

[13] (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (b) Grushin, V. V.; Akhrem, I. S.; Vol'pin, M. E. *J. Organomet. Chem.* **1989**, *371*, 403.

running the decomposition of **3** in the presence of iodobenzene, which furnished $[(Ph_3P)_2Pd(I)Ph]$[14] in quantitative yield.

The thermal decomposition of binuclear **1** in benzene or toluene starts at 50−55 °C to give CO_2, PhH, Pd metal, and a mixture of $[(Ph_3P)_3Pd]$ and $[(Ph_3P)_4Pd]$ in a ca. 2:1 ratio.[15] It is noteworthy that thermal decomposition reactions of **1** and **2** exhibit a well-pronounced autocatalytic effect which is due to the release of free phosphine in the course of the reaction.[16] The free phosphine adds to as yet unreacted **1** (eq 1) to give the more labile mononuclear **3**. This significant difference in stability of the monomeric and dimeric formates is a consequence of the facile attainment of the transition state **A**[8b] for **3** and **4** bearing η^1-formato ligands, whereas cleavage of the η^2-formato bridges in **1** and **2** is required before β-elimination can occur.



A

As anticipated, no autocatalytic effect was observed when the decomposition of **1** was conducted in the presence of iodobenzene (eq 3) since the presumably generated $[(Ph_3P)Pd]$ was trapped with PhI prior to decomposition.

$$\mathbf{1} \xrightarrow[-CO_2,\ -PhH]{\Delta} 2[(Ph_3P)Pd] \xrightarrow{2PhI} \underset{\mathbf{5}}{[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}I)_2]} \quad (3)$$

Only traces of Pd metal, if any, were formed in the course of reaction 3, which furnished $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}I)_2]$[9] (**5**) in quantitative yield. Therefore, oxidative addition of PhI to the highly coordinately unsaturated $[(Ph_3P)Pd]$ is substantially faster than the disproportionation to Pd metal and $[(Ph_3P)_nPd]$ (n = 3, 4). No noticeable difference was observed when reaction 3 was carried out in the absence, or in the presence, of 1,1-diphenylethylene (5-fold excess) as a radical trap.[17] This observation provides evidence against a free-radical mechanism for both the decomposition of **1** and the oxidative addition of PhI to the generated Pd(0) species.

A remarkable exchange between the σ-methyl groups and phenyls of the PPh_3 ligands was observed in the course of the thermal decomposition of **2** in toluene at 55 °C. A similar aryl/aryl exchange reaction[18] likely took place when **1** decomposed under the same conditions, but because of its degenerate nature this exchange was not detected. Two singlets at −0.5 and 22.0 ppm (3:1 integral intensity) were observed in the ^{31}P NMR spectrum when **2**, in toluene, was decomposed at 55 °C. Cooling this solution down to −92 °C resulted in transformation of the downfield signal into a singlet at 22.7 ppm and a doublet at 23.2 ppm with $J(P-P) = 94.5$ Hz, whereas a number of resonances in the range of 0−2 ppm replaced the singlet (−0.5 ppm) originally observed at 55 °C. The major low-temperature upfield resonance was a 1:2:1 triplet at 0.9 ppm, with the same coupling constant and half the intensity of the simultaneously observed doublet at 23.2 ppm. Clearly, the singlet at 22.7 ppm was due to $[(Ph_3P)_3Pd]$,[15b] whereas the doublet (23.2 ppm) and the triplet (0.9 ppm) appeared from an AB_2 spin system such as $[(Ph_3P)_2(Ph_2PMe)Pd]$. Unambiguous evidence for the methyl/phenyl exchange was observed by monitoring (^{13}C NMR) the decomposition of $[(Ph_3P)_2Pd_2(^{13}CH_3)_2(\mu\text{-}H^{13}COO)_2]$ (**2a**) in benzene-d_6 at 55 °C. In addition to the singlets at −4.3 ppm ($^{13}CH_4$) and 125.1 ppm ($^{13}CO_2$),[19] a very broad, intense resonance at 14 ppm and two sharp doublets at 16.8 ppm (major, $J(C-P) = 73.5$ Hz) and 18.3 ppm (minor, $J(C-P) = 71.6$ Hz) were observed in the ^{13}C NMR spectrum after the decomposition of **2a**. While the broad resonance could be assigned to various Pd(0) methylphosphine complexes in rapid exchange (see above), the doublets were clearly due to $Ph_2P(^{13}CH_3)O$ and $PhP(^{13}CH_3)_2O$,[20] respectively, which likely formed due to the traces of molecular oxygen present in the sample. No evidence was obtained for the formation of any $[L_2Pd(CO_2)]$ (L = tertiary phosphine) complexes, which are stable only under excess CO_2 at low temperature.[21]

The methyl/phenyl exchange process was totally suppressed when the thermolysis of **2** or **2a** was carried out in the presence of PhI or MeI at the same temperature. Thus, complex **6** formed quantitatively upon decomposition of **2** in benzene containing methyl iodide (eq 4).

$$\mathbf{2} \xrightarrow[-CO_2,\ -MeH]{\Delta,\ MeI} \underset{\mathbf{6}}{[(Ph_3P)_2Pd_2Me_2(\mu\text{-}I)_2]} \quad (4)$$

When **2** was decomposed in the presence of PhI, surprisingly both **5** and **6** were formed (in 100% overall yield), with the ratio of **5** to **6** being dependent on the concentration of iodobenzene. Quite striking was also the fact that higher concentrations of PhI resulted in lower ratios of **5** to **6**! In other words, the more PhI that was present, the less the σ-Ph complex formed. For instance, when the molar ratio of PhI to **2** was varied from 2.4 to 21, and further to ∞ (decomposition in pure iodobenzene), the observed (^{31}P NMR) ratios of **5** to **6** were 2.4, 1.9, and 1.6, respectively. Even more pronounced was the influence of the iodomethane concentration on the result of its reaction with **1** in benzene at 60 °C: the ratios of **5** to **6** were found to be 1.7 and 13.1 for the MeI to **1** molar ratios of 19 and ∞ (thermolysis in a 1:1 by volume mixture of MeI and benzene), respectively. These results can be rationalized in terms

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[14] Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

[15] (a) This ratio was determined by measuring the ^{31}P NMR spectrum of the decomposed 1 in toluene at −90 °C, the chemical shifts of the tri- and tetracoordinate Pd(0) complexes being 22.2 and 17.0 ppm.[15b] (b) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1673.

[16] At ambient temperature, $[(Ph_3P)_4Pd]$ is completely dissociated in solution to $[(Ph_3P)_3Pd]$ and PPh_3. See ref 15b and: Kurran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187.

[17] See for example: Lubinkowski, J. J.; Gomez, M.; Calderon, J. L.; McEwen, W. E. *J. Org. Chem.* **1978**, *43*, 2432. Grushin, V. V.; Shcherbina, T. M.; Tolstaya, T. P. *J. Organomet. Chem.* **1985**, *292*, 105.

[18] Kong, K.-C.; Cheng, C.-H. *J. Am. Chem. Soc.* **1991**, *113*, 6131. See also: Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

[19] Günther, H. *NMR Spectroscopy: An Introduction*; Wiley: New York, 1980; p 398.

[20] Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Org. Chem.* **1975**, *40*, 3437.

[21] Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Organometallics* **1994**, *13*, 407.

Scheme 1

$$\begin{tikzcd}
{[L_2Pd_2R_2(HCOO)_2]} \arrow[r, "\Delta", "-2CO_2"'] & {[L_2Pd_2R_2(H)_2]} \arrow[r, "-2RH"'] \arrow[d, "-2R'H"', "2R'I"] & {2[LPD]} \arrow[d, "2R'I"] \\
 & {[L_2Pd_2R_2I_2]} & {[L_2Pd_2R'_2I_2]}
\end{tikzcd}$$

of two competing processes shown in Scheme 1. Before the reductive elimination of RH occurs, the Pd hydrido intermediate may reduce the organic iodide, thus giving the "anomalous" metal product. As the reduction should be of positive order in the organic iodide, an increase of [R'I] would favor its reduction rate, thus decreasing the "normal" to "anomalous" product ratio.[22] These results shed light on the intimate process of the palladium-catalyzed reductive dehalogenation of haloarenes with formate anion,[3] indicating that *two* different mechanisms (Scheme 1; R = R') equally resulting in the arene production, can govern the catalytic process.

In conclusion, organopalladium formato complexes have been isolated and fully characterized for the first time. The facile thermal decomposition of these complexes results in smooth and clean generation of the highly reactive, coordinatively unsaturated species $[(Ph_3P)_nPd]$ (n = 1, 2). An investigation of the thermolysis of organopalladium formates, in the presence of organic iodides, disclosed the existence of two distinct mechanisms for the Pd-catalyzed reductive dehalogenation of aryl halides with formate anion.

Experimental Section

Physical measurements were carried out using the following equipment: Varian XL 300 (^{1}H, ^{13}C, and ^{31}P NMR), Bomem MB-100 (FT-IR), and Rigaku AFC6S (X-ray diffraction). All chemicals were purchased from commercial sources (Aldrich, Strem, and Organometallics) and used as received.

Synthesis of $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-}OH)_2]$. A mixture of $[(Ph_3P)_2PdCl_2]$ (1.10 g; 1.57 mmol), 50% KOH (4 g), benzene (8 mL), and MeI (1 mL) was stirred under nitrogen at room temperature for 20 h. The reaction mixture first turned dark brown and then gradually decolorized, and colorless precipitate formed. The workup was performed in air. Water (15 mL) and dichloromethane (50 mL) were added, the mixture was stirred until all the solid dissolved, and the organic layer was separated and evaporated. The residual oil was dried under vacuum and then stirred under nitrogen with dichloromethane (10 mL) and 50% KOH (8 g) for 3 h (small amounts of Pd metal precipitated). The yellow organic phase was separated, filtered through cotton, and evaporated. The residue was dried under vacuum until solidified, and treated with acetone (4 mL), to give a grayish white microcrystalline solid which was thoroughly washed with acetone (3 × 3 mL) and dried under vacuum. The yield of $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-}OH)_2]$ (monohydrate) was 0.46–0.58 g (70–90%). In chloroform solution, the complex exists as a 1:1 mixture of cis and trans isomers. ^{1}H NMR ($CDCl_3$; δ): −3.3 (br s, 0.5H, cis-OH); −2.1 (br s, 1H, trans-OH); −0.7 (br s, 0.5H, cis-OH); 0.0 (d, 3H, J = 2.6 Hz, Pd−CH_3); 0.2 (d, 3H, J = 2.6 Hz, Pd−CH_3); 7.5 (m, 30H, C_6H_5). ^{31}P ($CDCl_3$; δ): 39.4 (s, 0.5P); 39.6 (s, 0.5P). IR (Nujol; cm^{-1}): 3610 (OH). Anal. Calcd for $C_{38}H_{40}O_3P_2Pd_2$: C, 55.7; H, 4.9. Found: C, 55.7; H, 4.9.

Synthesis of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}HCOO)_2]$ (1). Formic acid (30 mg; 0.65 mmol) was added to a stirred mixture of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ (0.20 g; 0.22 mmol) and benzene (8 mL), causing immediate dissolution of the solid. The resulting benzene solution was filtered, reduced in volume to ca. 2 mL (the temperature of the bath should not exceed 35 °C), and treated with hexane (dropwise) until the solution grew turbid. After some crystals formed, more hexane (25 mL) was added, and the mixture was kept at −17 °C for 1 h. The yellowish crystals were separated, washed with hexane (3 × 3 mL), and dried under vacuum. The yield of **1** was 0.193 g (91%). Anal. Calcd for $C_{50}H_{42}O_4P_2Pd_2$: C, 61.2; H, 4.3. Found: C, 61.5; H, 4.5. ^{1}H NMR (benzene-d_6, 18 °C; δ): 7.0 (m, 18H, 3,4,5-C_6H_5P); 7.1 (m, 6H, 3,4,5-C_6H_5Pd); 7.65 (m, 12H, 2,6-C_6H_5P); 7.85 (m, 4H, 2,6-C_6H_4Pd); 8.3 (s, 2H, HCOO). ^{31}P NMR (C_6H_6; δ): 30.3 (s). IR (Nujol; cm^{-1}): 2825 (shoulder; H−COO); 1593, 1353 (CO).

Synthesis of $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-}HCOO)_2]$ (2). Formic acid (45 mg; 1 mmol) was added to a stirred suspension of $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-}OH)_2]\cdot H_2O$ (0.23 g; 0.28 mmol) in benzene (10 mL). The solid dissolved immediately, and the mixture was stirred for another 5 min. The yellow benzene solution was filtered and reduced in volume to 2–3 mL (the temperature of the bath should not exceed 35 °C). Hexane was added dropwise until the solution turned cloudy, and the mixture was left until a considerable amount of yellowish crystals formed (10–20 min). More hexane (15 mL) was added portionwise; the crystals were separated, washed with hexane (3 × 4 mL), and dried under vacuum. The yield of **2**$\cdot 1.5C_6H_6$ was 0.252 g (92%). Anal. Calcd for $C_{49}H_{47}O_4P_2Pd_2$: C, 60.4; H, 4.9. Found: C, 60.3; H, 5.0. ^{1}H NMR ($CDCl_3$, 18 °C; δ): 0.65 (s, 6H, CH_3); 7.3 (m, 18H, 3,4,5-C_6H_5); 7.6 (m, 12H, 2,6-C_6H_5); 7.95 (br s, 2H, HCOO). ^{31}P NMR (C_6H_6; δ): 37.8 (s). IR (Nujol; cm^{-1}): 2810 (H−COO); 1595, 1349 (CO).

Complex **2a** was prepared similarly from $[(Ph_3P)_2PdCl_2]$, $^{13}CH_3I$, and $H^{13}COOH$. ^{13}C NMR (benzene-d_6, 18 °C; δ): 3.1 (s, $^{13}CH_3$), 170.6 (s, $H^{13}COO$).

Synthesis of $[(Ph_3P)_2Pd(Ph)(HCOO)]$ (3). Formic acid (45 mg; 1 mmol) was added to a stirred mixture of $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ (0.125 g; 0.135 mmol) and benzene (4 mL). After the solid dissolved, the resulting lemon yellow benzene solution was filtered, reduced in volume to ca. 2 mL (the temperature of the bath should not exceed 35 °C), and treated with PPh_3 (0.10 g; 0.38 mmol) at 5–10 °C (ice bath). The addition of triphenylphosphine caused immediate decolorization of the solution. While the mixture was kept in the ice bath, cold (0–5 °C) hexane was added dropwise until the solution turned cloudy. After colorless, well-shaped crystals started growing, more cold hexane (10 mL) was added portionwise, and the mixture was kept at ca. 0 °C for 1 h. The crystals were separated, washed with hexane, and dried under vacuum at room temperature. The yield of **3** was 0.20 g (98%). Anal. Calcd for $C_{43}H_{36}O_2P_2Pd$: C, 68.6; H, 4.8. Found: C, 69.1; H, 4.9. ^{1}H NMR (benzene-d_6, 7 °C; δ): 6.5 (m, 3H, 3,4,5-C_6H_5Pd); 6.7 (m, 2H, 2,6-C_6H_5Pd); 7.1 (m, 18H, 3,4,5-C_6H_5P); 7.85 (m, 12H, 2,6-C_6H_5P); 8.25 (s, 1H, HCOO). ^{31}P NMR (C_6H_6, 7 °C; δ): 22.0 (s). IR (Nujol; cm^{-1}): 2803 (H−COO); 1609, 1313 (CO).

Synthesis of $[(Ph_3P)_2Pd(Me)(HCOO)]$ (4). Formic acid (45 mg; 1 mmol) was added to a suspension of $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-}OH)_2]\cdot H_2O$ (0.115 g; 0.14 mmol) in benzene (2 mL), with stirring. After the solid dissolved, the yellow benzene solution was separated, the flask was rinsed with benzene (1 mL), and the combined benzene solutions were filtered and placed on an ice bath. When benzene started crystallizing, PPh_3 (0.11 g; 0.42 mmol) was added, and the mixture was carefully warmed and stirred until the crystallized benzene melted and the PPh_3 dissolved. Cold (0 °C) hexane (3 mL) was added, and the mixture was kept at −17 °C until yellowish crystals started

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[22] It is conceivable that the intermediate organopalladium hydrido species and the already formed organopalladium iodides undergo an intermolecular σ-Me/σ-Ph exchange similar to that described for the cross-coupling reactions of diorganopalladium complexes and organic halides.[23] We thank a reviewer for bringing this possibility to our attention.

[23] Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144. Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *330*, 253. Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180.

depositing. More hexane (2 mL) was added, and the mixture was kept at −17 °C for another 1 h, after which the crystals were separated, washed with hexane, and dried under vacuum. The yield of the spectroscopically (^{1}H, ^{31}P NMR) pure **4** was 0.138 g (85%). Satisfactory elemental analysis was not obtained due to the instability of the complex at ambient temperature. ^{1}H NMR (benzene-d_6, 7 °C; δ): 0.55 (t, 3H, J(H−P) = 6.2 Hz), CH_3); 7.2 (m, 18H, 3,4,5-C_6H_5); 8.0 (m, 12H, 2,6-C_6H_5); 8.2 (s, 1H, HCOO). ^{31}P NMR (benzene, 7 °C; δ): 29.7 (s). IR (Nujol; cm^{-1}): 2787 (H−COO); 1606, 1302 (CO).

Decomposition of 2 in the Presence of MeI (Synthesis of 6). An oxygen-free mixture of **2**·1.5C_6H_6 (70 mg; 0.07 mmol), benzene (5 mL), and MeI (0.5 mL) was heated at 60 °C in a closed flask under N_2 for 2 h. The brownish solution was filtered hot and evaporated, and the residue was treated with acetone to give 60 mg (82%) of brownish **6**, which was washed with acetone and dried under vacuum. Anal. Calcd for $C_{38}H_{36}I_2P_2Pd_2$: C, 44.7; H, 3.6. Found: C, 45.1; H, 3.6. ^{1}H NMR ($CDCl_3$, 18 °C; δ): 0.8 (d, 6H, J(H−P) = 3.2 Hz, CH_3); 7.4 (m, 18H, 3,4,5-C_6H_5); 7.65 (m, 12H, 2,6-C_6H_5). ^{31}P NMR (C_6H_6, 18 °C; δ): 38.0 (s).

Synthesis of [$(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}CH_3COO)_2$]. Acetic acid (35 mg; 0.58 mmol) was added to a stirred mixture of [$(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2$] (0.17 g; 0.18 mmol) and benzene (6 mL), causing fast dissolution of the solid. The resulting benzene solution was evaporated, and the residual crystals were washed with hexane and dried under vacuum. The yield of [$(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}CH_3COO)_2$]·1.5$C_6H_6$ was 0.204 g (98.5%). Anal. Calcd for $C_{61}H_{55}O_4P_2Pd_2$: C, 65.0; H, 4.9. Found: C, 65.0; H, 4.9. ^{1}H NMR (benzene-d_6, 18 °C; δ): 1.6 (s, 6H, CH_3); 7.0 (m, 24H, 3,4,5-C_6H_5); 7.5 (m, 12H, 2,6-C_6H_5P); 7.8 (m, 4H, 2,6-C_6H_5Pd). ^{31}P NMR (C_6H_6; δ): 30.4 (s). IR (Nujol; cm^{-1}): 1580, 1377 (CO).

Synthesis of [$(Ph_3P)_2Pd(Ph)(CH_3COO)$]. A mixture of [$(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}CH_3COO)_2$]·1.5$C_6H_6$ (0.08 g; 0.07 mmol), benzene (5 mL), and PPh_3 (0.055 g; 0.21 mmol) was stirred at room temperature for a few minutes until all the solid dissolved and a clear, colorless solution formed. The solution was reduced in volume to ca. 2 mL, and the residue was treated with hexane (10 mL, portionwise). After 1 h, the colorless crystals were separated, washed with hexane, and dried under vacuum. The yield of [$(Ph_3P)_2Pd(Ph)(CH_3COO)$] was 0.106 g (97%). Anal. Calcd for $C_{44}H_{38}O_2P_2Pd$: C, 68.9; H, 5.0. Found: C, 68.9; H, 4.9. ^{1}H NMR (benzene-d_6; δ): 1.4 (s, 3H, CH_3); 6.4 (m, 3H, 3,4,5-C_6H_5Pd); 6.6 (m, 2H, 2,6-C_6H_5-Pd); 7.0 (m, 18H, 3,4,5-C_6H_5P); 7.7 (m, 12H, 2,6-C_6H_5P). ^{31}P NMR (C_6H_6; δ): 21.7 (s). IR (Nujol; cm^{-1}): 1605, 1324 (CO).

Single-Crystal Diffraction Study of 2·1.5C_6H_6. A well-shaped crystal of **2**·1.5C_6H_6 having approximate dimensions of 0.2 × 0.2 × 0.2 mm was mounted on a glass capillary. The measurements were made at −130 °C with Mo Kα radiation and a graphite monochromator. During the data collection, standard reflections were measured after every 150 reflections to check the stability of the crystal. No crystal decay was noticed. A total of 5025 reflections were measured. The unique set contained 4633 reflections. Using the criterion $I > 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from the counting statistics, 4067 out of 5025 reflections were used. The data were corrected for Lorentz and polarization effects.[24] An absorption correction (ψ-scan) was made. The minimum and maximum transmission factors were 0.8168 and 0.8175.

The structure was solved by direct methods. All the atoms were refined anisotropically, except for the hydrogens. The hydrogen atoms were found by a difference Fourier map. To increase the ratio of reflections to parameters, the benzene rings were all refined as rigid groups. One of the solvent molecules (C(47)−C(52)) has an occupancy of 0.5, and the other one (C(41)−C(46)) has an occupancy of 1. The value of 0.5 (confirmed by elemental analysis, see above) was obtained by refining the occupancy and fixing the thermal parameter to a value close to that of the other solvent molecule. There were still some residues around the solvent molecule with an occupancy of 0.5, which could be due to a small disorder. The final cycle of full-matrix least-squares refinement was based on 4067 observed reflections and 416 parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final Fourier map corresponded to 0.960 and −0.620 e/Å^3, respectively. All the calculations were performed using the NRCVAX crystallographic software package.[25]

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Supporting Information Available: Tables and text giving X-ray crystallographic data for **2**·1.5C_6H_6 (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(24) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

(25) Gabe, E. J.; Lee, F. L.; Le Page, Y. *J. Appl. Crystallogr.* **1989**, *22*, 384.