was monitored by an in-stream thermocouple which had been previously calibrated against a second thermocouple in the sample position. Automatic peak search and indexing procedures yielded the monoclinic reduced primitive cell. The final cell parameters and specific collection parameters are given in Table 7.

The 4143 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.75$ for the average curve. An empirical correction for absorption, based on the azimuthal scan data, was applied to the intensities since it was not possible to accurately measure the sample crystal. Removal of systematically absent and redundant data left 3775 unique data.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the expected positions of most of the hydrogen atoms were found. A difference Fourier map calculated after inclusion of all other hydrogen atoms clearly showed the position of the hydride ligand attached to the metal. All hydrogen atoms were then allowed to refine with isotropic thermal parameters. A secondary extinction parameter was refined in the final cycles of least-squares. The final residuals for 267 variables refined against the 3100 data for which $F^2 > 3|F^2|$ were $R = 2.04\%$, $wR = 2.53\%$, and GOF = 1.356. The R value for all 3775 data was 3.49%.

The quantity minimized by the least-squares program was $w(|F_0| - |F_c|)^2$ where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.025 in the last cycles of the refinement. The analytical forms of the scattering factor tables of the neutral atoms were used, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of sin $(\theta)/\lambda$, $|F_0|$, and parity and value of the individual indices showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 2.14 $e^-/Å^3$ and was located only 0.74 Å from the iridium atom. All other peaks in the final difference Fourier map had densities of less than 1 $e^-/Å^3$. The positional parameters of the atoms and the estimated standard deviations are given in Table 8. Structure factor amplitudes were provided as supplementary material in the preliminary communication.[4]

Acknowledgment. This work was carried out under the auspices of a collaborative Lawrence Berkeley Laboratory/Industrial research project supported jointly by the Chevron Research Company, Richmond, CA, and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We are also grateful for helpful discussions with Drs. J. A. Labinger and J. T. Groves and for a loan of iridium chloride from the Johnson-Matthey Corp. We thank Sue Rossi for Figure 7.

Synthesis and Reactions of Dinuclear Palladium Complexes Containing Methyls and Hydride on Adjacent Palladium Centers: Reductive Elimination and Carbonylation Reactions

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Abstract: The transmetalation reaction of trimethylaluminum with the palladium chloride dimer $Pd_2Cl_2(\mu\text{-dppm})_2$ (**1**) (dppm = bis(diphenylphosphino)methane) at −78 °C gave an intermediate, $Pd_2ClMe(\mu\text{-dppm})_2$ (**2**), which disproportionated at ~10 °C to yield the trans-face-to-face palladium dimer $Pd_2Cl_2Me_2(\mu\text{-dppm})_2$ (**3**) and a palladium dimer $Pd_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2$ (**5**). The use of excess trimethylaluminum at −40 °C gave the dimethyl complex, $Pd_2Me_2(\mu\text{-dppm})_2$ (**7**). When **2** and **7** were protonated, a stable A-frame chloro-bridged dimer $[Pd_2HMe(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ (**6**) and a hydride-bridged dimer $[Pd_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (**8**) were obtained. Warming **6** in solution to ambient temperature caused the reductive elimination of methane; **8** lost methane and ethane at ambient temperatures. Both reductive eliminations were strictly intramolecular as determined by crossover experiments. The reaction of **6** with CO (1 atm) at −20 °C first gave a carbonyl-bridged complex $[Pd_2Me(H)(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2]^+$ (**10**) that rearranged to the acyl complex $[Pd_2H(COCH_3)(\mu\text{-Cl})(\mu\text{-dppm})]^+$ (**11**) and then on warming eliminated acetaldehyde. The carbonylation of **8** (1 atm) proceeded stepwise to give first the mono- and then the diacyl complexes. The diacyl complex $[Pd_2(COCH_3)_2(\mu\text{-H})(dppm)_2]^+$ (**13**) underwent the reductive elimination of acetaldehyde at ambient temperatures.

Metal dimers are the simplest conceptual models of metal surfaces in catalysts but have the advantage that because of their relatively good solubility, a study of their reactions is comparitively simple.[1] The mechanistic features of the reactions of organic fragments on metal dimers or clusters can be established more readily than those of reactions taking place on surfaces, at least with the present state of the available methods and physical characterization techniques.[2]

There are a number of reactions of metal dimers and clusters that are unique in their mode of transformation and bonding as compared to homogeneous catalysts containing a single metal atom.[1,3] It has been suggested that the lack of reactivity in some of the more difficult reactions such as methanation and the Fischer–Tropsch syntheses may be due to the requirement for multinuclear centers to activate the substrate sufficiently.[1,4] Nevertheless, there is relatively little chemistry resulting in the generation of organic products that has been observed in stoi-

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(2) See, for example: "Metal Clusters in Catalysis" In *Studies in Surface Science and Catalysis*; Gates, B. C., Guczi, L., Knozinger, H., Eds.; Elsevier: New York, 1986; Vol. 29.

(3) See, for example: (a) Dombek, B. D. *Organometallics* **1985**, *4*, 1707. (b) Beanan, L. R.; Keister, J. B. *Ibid.* **1985**, *4*, 1713.

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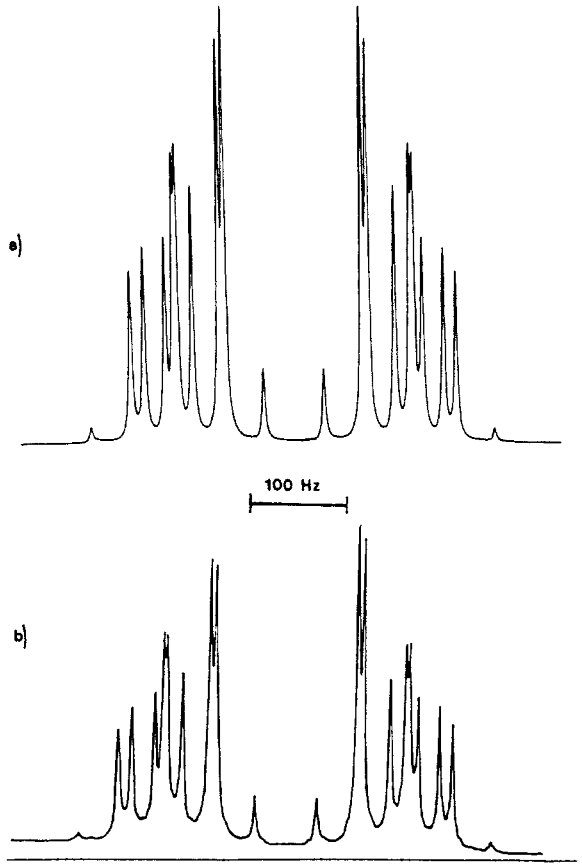

Figure 1. $^{31}P\{^1H\}$ NMR (81.015 MHz) of **2**: (a) simulated spectrum and (b) spectrum of **2** at -80 °C in CD_2Cl_2.

chiometric or catalytic reactions of dimers, particularly with the late transition metals where the catalysis of organic reactions abounds.

We report herein the synthesis of palladium dimers containing methyl and hydride groups, the thermal reductive elimination of these groups, the reactions of these organometallic dimers with carbon monoxide, and the subsequent reductive elimination of acetaldehyde from the resulting acylsubstituted dimers.

Results and Discussion

Synthesis of Palladium Dimers Containing Methyl and Hydride. Although a relatively large number of dinuclear platinum complexes containing two bridging bis(diphenylphosphino)methane (dppm) ligands and alkyl groups σ-bonded to platinum are known,[5-8] there are relatively few examples of similar dinuclear palladium complexes,[9,10] and none of the palladium dimers contain both an alkyl group and a hydride.

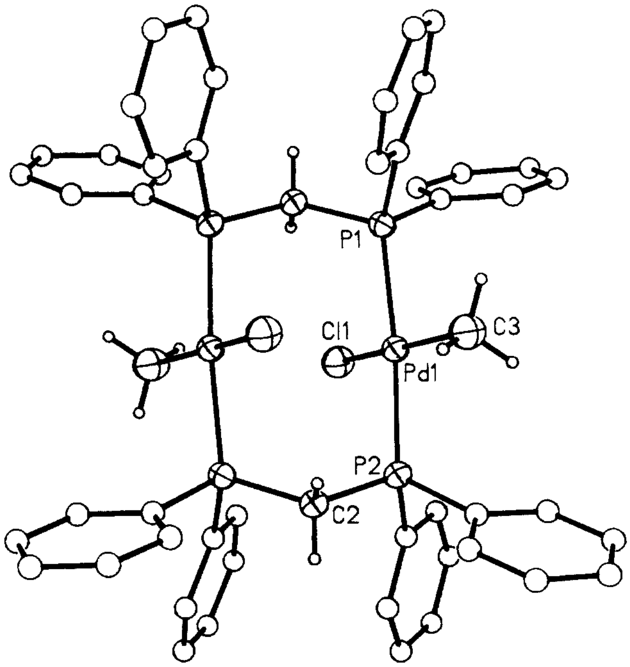

Figure 2. X-ray structure of **3**.

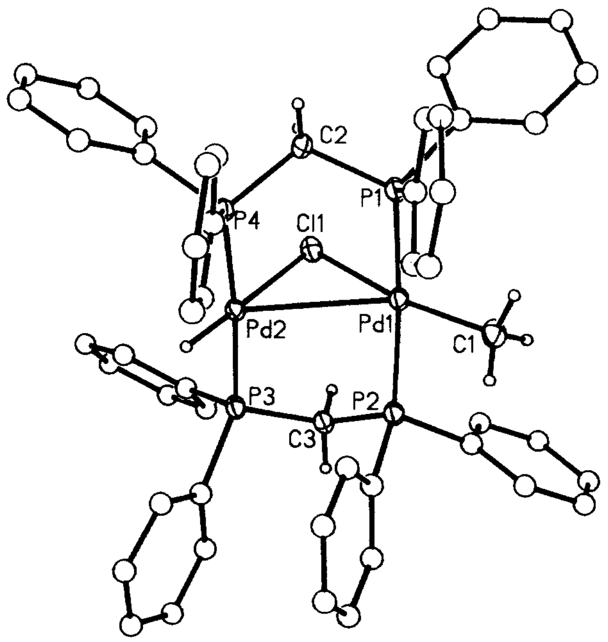

Figure 3. X-ray structure of **6-H**.

The reaction[11] of an equimolar amount of trimethylaluminum with the palladium(I) chloride dimer $Pd_2Cl_2(dppm)_2$ (**1**)[12] at -78

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°C in methylene chloride replaced one chlorine with methyl to give a quantitative yield of an unstable complex **2** which could not be isolated (Scheme I) but was characterized by its ^{1}H and ^{31}P{^{1}H} spectra. The ^{31}P{^{1}H} spectrum of **2**, analyzed as an AA′BB′ spin system, is shown (Figure 1) along with the calculated spectrum. The ^{1}H NMR spectrum of **2** showed the methyl group attached to palladium as a triplet at 0.2 ppm.

At ambient temperature, **2** disproportionated to a palladium(0) complex (presumably **4**) and **3** (70% yield); the X-ray structure of **3** (Figure 2) showed a face-to-face dimer with the methyl groups in the anti geometry. The Pd–Pd distance (3.381 (1) Å) in **3** is consistent with the absence of any appreciable metal–metal bonding interaction, as expected from the formal electron count for these atoms.

The palladium(0) complex **4**, which could be detected in solution (^{31}P{^{1}H} = 22 ppm), reacted with methylene chloride to give a quantitative yield of the A-frame methylene-bridged dimer **5**. The reactions of methylene chloride with $Pd_2(dppm)_3$ to form **5** had been reported to proceed only very slowly.[9,10b] A faster reaction occurs with **4**, apparently because it is a more coordinatively unsaturated palladium(0) species.

The dimeric dimethyl palladium(II) complex containing chlorides is not available directly from the oxidative addition of methyl chloride to $Pd_2(dppm)_3$;[10b] only the corresponding dibromide and diiodide have been obtained from the oxidative addition reactions.

The palladium(I) complex **2** having methyl and chloride on adjacent palladium atoms was converted, at −78 °C, to the cationic complex **6-H** by the addition of ethanol to the reaction mixture. Presumably ethanol generates some HCl by its reaction with the dimethylaluminum chloride product present in the reaction mixture, and the HCl protonates **2**. Complex **6-H**, containing methyl and hydride on different palladium atoms and a chloride counter ion was somewhat unstable (vide infra); however, complex **6-H** containing the tetraphenyl borate counter ion was more stable, could be isolated in an 85% yield from **2**, and was fully characterized, including its X-ray structure (Figure 3). The Pd–Pd distance in **6-H** (3.031 (1) Å) supports the existence of the metal–metal interaction shown. The hydride ligand was located , and its position was refined; the final Pd2–H1 distance was 1.53 (5) Å. The ^{1}H NMR spectrum of **6-H** showed the hydride at −12.42 ppm and the palladium methyl at 0.65 ppm.

When the reaction of **1** with trimethylaluminum was carried out at −78 °C with a 20-fold excess of the aluminum reagent and then allowed to warm to −40 °C, the dimethyl palladium(I) dimer **7** was obtained, as evidenced by the observation in the ^{1}H NMR spectrum of the methyls attached to palladium at 0.45 ppm. This dimethyl palladium(I) dimer was converted to the hydride-bridged dimer **8** containing methyls on the palladiums by the addition of ethanol to the reaction mixture. Cationic complex **8** was isolated analytically pure in 70% yield as its tetraphenylborate salt. The ^{1}H NMR spectrum of **8** revealed the methyls attached to palladium at 0.07 ppm and the bridged hydride at −7.55 ppm. Complex **8** could be recrystallized from methylene chloride, and crystals apparently suitable for X-ray diffraction study were obtained. However, in the course of recrystallization, some of the hydride was replaced by chloride and the two isostructural compounds cocrystallized. The X-ray diffraction study (see Experimental Section) not only confirmed the basic structure of **8** but also showed that a small percentage (approximately 15%) of the bridging hydride ligand had been replaced by chloride ion.

Reductive Elimination Reactions of 6 and 8. When a solution of **6-H** containing the chloride counterion was warmed to −20 °C, methane was evolved quantitatively, and an 80% yield of the palladium(I) chloride dimer **1** was isolated. When **6-H** (as its tetraphenylborate salt) was warmed to (40–55 °C) in solution, the quantitative evolution of methane occurred, producing 33% yields of both **1** and the face-to-face dimer **3**. However, the addition of LiCl to the solution of the tetraphenylborate salt of **6-H** allowed the reductive elimination to take place at lower temperatures (−20 °C). In no case was ethane or dihydrogen evolved (NMR, GC, mass spectrum).

The corresponding deuteriated complex (**6-D**) containing deuteride on one palladium and trideuteriomethyl on the other was prepared with perdeuteriotrimethylaluminum[13] and ethanol-d_1. Reductive elimination from **6-D** gave a quantitative yeild of CD_4. A solution containing equimolar amounts of **6-H** and **6-D** produced only CH_4 and CD_4 (m/e 20, 16 but no 19). Thus, the reductive elimination is strictly intramolecular.

Warming (25–45 °C) a methylene chloride solution of complex **8-H**, which contains methyls on the two palladiums and a hydride bridge, caused the evolution of both methane *and ethane* in an ~2:1 ratio and produced both the face-to-face dimer **3** and the A-frame dimer **5** in addition to an unidentified complex and free dppm. The corresponding deuteriated complex (**8-D**) containing trideuteriomethyls and a deuteride bridge was prepared with perdeuteriotrimethylaluminum[13] and ethanol-d_1. Warming a solution containing equimolar amounts of **8-H** and **8-D** also generated a 2:1 mixture of methane and ethane. The ethane was CH_3CH_3 and CD_3CD_3; no crossover products were detected. The methane was composed of four products, CH_4 and CD_4 as well as the crossover products CH_3D and CD_3H. The ratios of CH_4 and CD_4 to the crossover products varied from experiment to experiment. Although the reductive elimination to produce ethane is intramolecular, the crossover in the case of the generation of ethane could arise as a result of the lability of the bridging hydride in **8**.

Intermolecular dinuclear reductive elimination mechanisms have been established for several reactions, but only rarely have the corresponding intramolecular eliminations been investigated.[7c] In principle, the coupling of metal-bonded organic groups can take place from adjacent metal atoms or from the same metal atom in the dinuclear complex.[14] Although dinuclear eliminations could arise by coupling from adjacent metals (1,2-dinuclear elimination), the mechanistic information available has not established this as the pathway.[15] The reaction is symmetry forbidden; extended Hückel calculations predict a minimum activation energy of approximately 65 kcal/mol for the elimination of dihydrogen from adjacent metals even when the hydrogen atoms undergo a prior bending toward each other to establish the final dihydrogen geometry.[15]

In both the reductive elimination reactions of **6** and **8**, a 1,1-reductive elimination pathway is possible, since a rapid rearrangement can place both groups on the same palladium. The two methylene protons on dppm in A-frame dimer **5** have different chemical shifts, but the methylene protons on dimers **6-H** and **6-D** are identical even at −100 °C. The fluctionality of these complexes provides a pathway for the reductive elimination of methane whereby methyl and hydride become attached to the same palladium. Of the number of mechanisms for the A-frame inversion of platinum complexes of the type $[Pt_2(\mu\text{-dppm})_2(\mu\text{-Y})X_2]$ that have been considered, inversion of hydride through the platinum–platinum center is that most consistent with the available data.[16] A rapid equilibrium (Scheme II) would account for the equivalence of the methylene hydrogens on dppm. The palladi-

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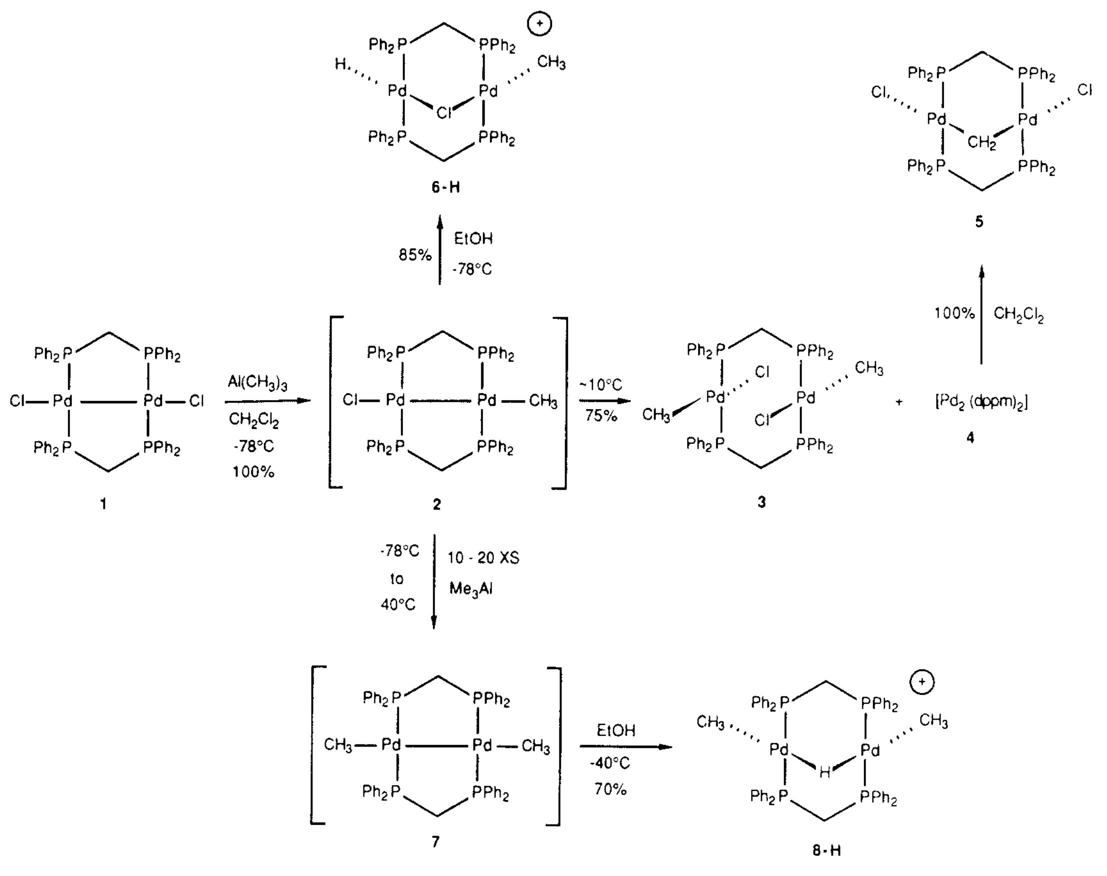
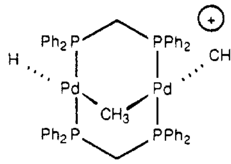
Scheme I



um–palladium distance in **6-H**, 3.03 Å, is sufficient to accommodate the inversion of hydride (Pd–H = 1.53 Å).[17] The equilibria (Scheme II) not only leads to the observed equivalence but also provides a mechanism by which hydride and methyl become bonded to the same palladium. The terminal bonding of chloride ion that is possible when it replaces tetraphenylborate apparently is effective in shifting the equilibrium to a complex with both methyl and hydride on the same palladium. The hydride and methyl ligands in complexes **6-H**$_b$ and **6-H**$_c$, however, are trans, and an isomerization to a cis complex would be required prior to reductive elimination,[18] probably by dissociation of one phosphine of dppm.

The ^{1}H NMR spectrum of **8-H** also shows equivalent methylene protons on the dppm ligand. In this complex, direct hydride inversion between the palladium atoms may be possible since the palladium–palladium distance in **8-H** is approximately 2.84 Å. However, a 1,1-reductive elimination of ethane requires two methyls requires two methyls on the same palladium. In order to accomplish this, a transient methyl bridged dimer **9** would be required, which could yield ethane after rearranging to complex in which the methyl groups are cis.



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Reaction of 6 and 8 with CO. Reaction of **6-H** (tetrafluoroborate) in methylene chloride with 1 atm of carbon monoxide at −22 °C first formed a carbonyl complex that appeared to be a bridged complex **10** (IR 1695 cm^{-1}; ^{1}H NMR δ 1.0, methyl; −11.3, hydride), which was not isolated but rearranged completely after 72 h to **11** (IR 1715 cm^{-1}; ^{1}H NMR δ 1.72, methyl; −10.02, hydride). At ambient temperature, **11** eliminated acetaldehyde to give **1**, the face-to-face dimer **3**, and an unidentified palladium carbonyl complex. The same reaction was observed in acetone, except that the CO insertion took place at −40 °C, and by the time the reaction temperature reached −20 °C, the reductive elimination was complete. When the reaction was carried out in acetone in the presence of added lithium chloride, CO insertion started as the solvent melted (~−95 °C). At −50 °C, a minor amount of what appeared to be a *formyl complex* was observed (^{1}H NMR δ 10.20) in the early stages of the reaction, along with acyl complex **11**. Complex **11** (chloride anion) cleanly decomposed in solution to yield acetaldehyde and **1**. Crystals of **10** could be isolated, but these decomposed in attempts to obtain an X-ray structure.

By treatment of **8-H** (tetraphenylborate) with 1 atm CO in methylene chloride at −22 °C, the stepwise insertion could be observed, first to form monoacyl complex **12** (IR 1701 cm^{-1}; ^{1}H NMR δ 1.64, acyl methyl; 0.15, palladium methyl) and finally after 48 h to yield diacyl complex **13** (IR 1708 cm^{-1}; ^{1}H NMR δ 1.68, acyl methyls). Warming **13** to ambient temperature produced acetaldehyde, chloroacetone (probably by the involvement of CH_2Cl_2), and a number of products containing palladium, including the face-to-face dimer **3**. No biacetyl was detected.

The reaction of 1 atm of CO (or less) with the palladium(I) dimer **1** is extremely rapid at ambient temperatures, giving the corresponding carbonyl bridged complex.[19] By contrast, the carbonylation of palladium dimers containing methyl but no hydride, $[Pd_2(dppm)_2(\mu\text{-}X)(CH_3)_2]^+$ (X = I, Br) and $[Pd_2(dppm)_2(\mu\text{-}I)CH_3I]^+$, takes place slowly at ambient temperature (45 psi, >3 days).[10c] Both **6-H** and **8-H** react with CO at lower temperatures with comparable or shorter reaction times. In addition, carbonylation of the halogen bridged dimers [Pd$_2$-

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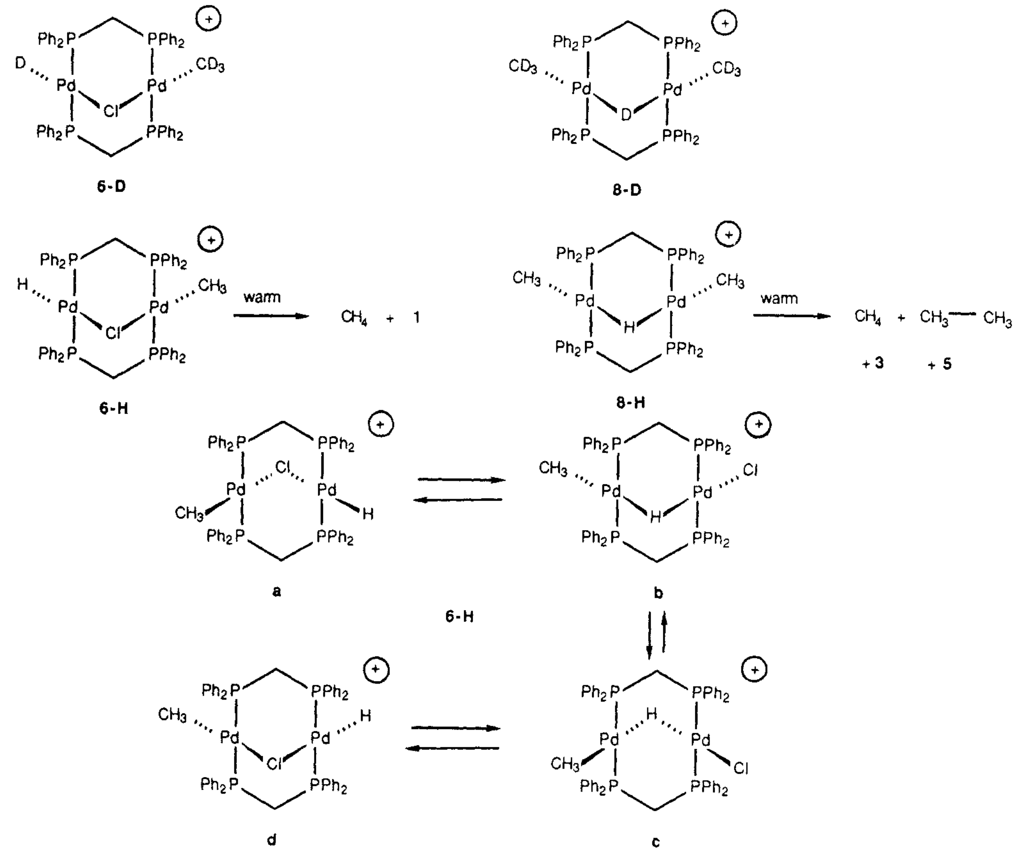
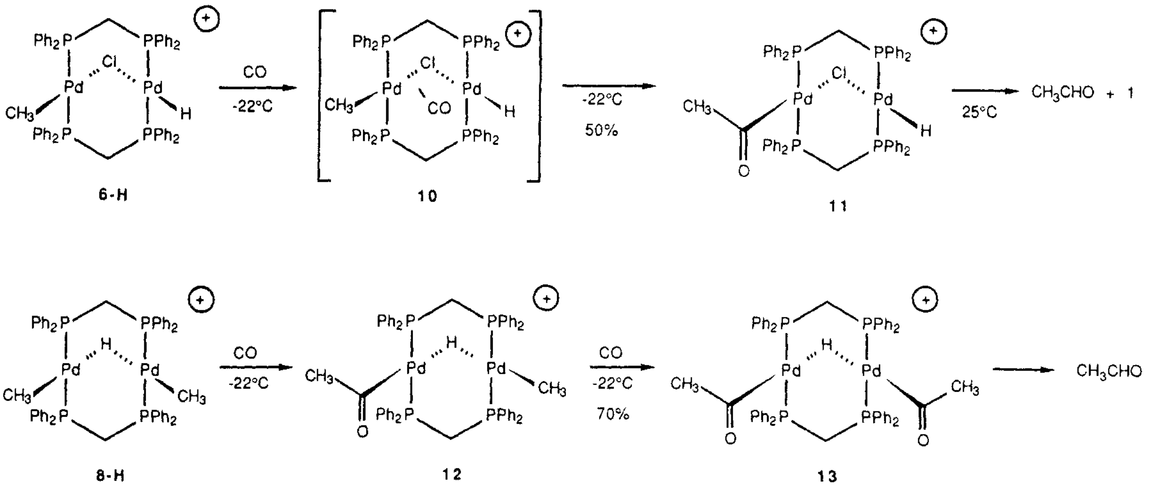
Scheme II



Scheme III



(dppm)$_2$(μ-X)(CH$_3$)$_2$]$^+$ and [Pd$_2$(dppm)$_2$(μ-I)CH$_3$I]$^+$ yields the corresponding acyl complexes that do not undergo spontaneous reductive elimination.[10c] The observation of a possible formyl complex in the early stages of the carbonylation in acetone at low temperatures in the presence of lithium chloride represents one of the few examples of straightforward CO insertion into a metal hydride bond.[20] The mechanism of the reductive elimination of acetaldehyde from **11** apparently is similar to that for the elimination of methane from **6**.

Experimental Section

Materials and Methods. Air-sensitive compounds were handled in Schlenk-type glassware on a dual manifold Schlenk line or in a Vacuum Atmospheres glovebox under an atmosphere of either prepurified argon or nitrogen. Solvents were rendered water- and oxygen-free by distillation at high vacuum from sodium benzophenone ketyl or dianion.

The ^{1}H and ^{31}P{^{1}H} spectra were recorded on an IBM WP-200 SY NMR spectrometer. Proton chemical shifts are in ppm and are relative to the residue proton solvent peaks. Phosphorus chemical shifts are relative to external H$_3$PO$_4$. IR spectra were recorded with a Perkin Elmer 983 spectrometer. Gas chromtography was performed with a Hewlett Packard 5750 research chromatograph. Mass spectra were recorded with a VG Micromass 16F spectrometer. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

The palladium(I) dimer Pd$_2$Cl$_2$dppm$_2$ (**1**) was prepared by literature procedures.[21] Carbon monoxide was predried by passing through a 4-Å

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Table I. The Crystallographic Experiments and Computations

compound	**3**	**6**
formula	$C_{52}H_{50}Cl_2P_4Pd_2$	$C_{78}H_{74}BCl_7P_4Pd_2$
formula wt, amu	1082.6	1607.2
temp, °C	20(1)	−130
cryst system	triclinic	triclinic
space group	$P1$	$P1$
a, Å	10.302 (1)	11.484 (3)
b, Å	11.169 (1)	17.714 (4)
c, Å	12.268 (2)	18.590 (8)
α, deg	65.88 (1)	77.51 (3)
β, deg	80.90 (1)	77.36 (3)
γ, deg	63.92 (1)	76.91 (2)
V, Å^3	1156.8	3535
Z	1	2
$F(000)$	548	1636
D(calcd), g cm^{-3}	1.55	1.61
cryst dim, mm	0.18 × 0.18 × 0.08	0.32 × 0.30 × 0.08
radiation	Mo Kα (λ = 0.7107 Å)	Mo Kα
monochromator	graphite	graphite
μ, cm^{-1}	10.45	8.95
scan type	$\theta/2\theta$	ω (Wyckoff)
2θ range, deg	3.5–50.0	3.5–50.0
indices collected	$-h,\pm k,\pm l$	$\pm h,\pm k,-l$
reflcns	4098 unique 3707 used ($I > 3\sigma(I)$)	11455 unique 10081 used ($I > 1.25\sigma(I)$)
scan spd, deg min^{-1}	variable (2–29)	variable (5–29)
no. least sq param	274	848
data/params	13.5	11.9
R^a	0.028	0.056
$R_w{}^a$	0.030	0.056
GOF^a	1.34	1.34
g (refined)	1.5×10^{-4}	4.0×10^{-4}

[a] $R = (\sum|(F_o - F_c)|)/(\sum F_o)$; $R_w = \{(\sum w|F_o - F_c|^2)/(\sum w(F_o)^2)\}^{1/2}$; $\mathrm{GOF} = \{(\sum w(|(F_o - F_c)|)^2)/(N_{\mathrm{data}} - N_{\mathrm{params}})\}^{1/2}$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)^a for **3**

atom	x	y	z	$U_{\mathrm{iso}}{}^b$
Pd1	8377 (1)	5343 (1)	−483 (1)	25 (1)
P1	8665 (1)	7202 (1)	−2111 (1)	26 (1)
C11	9404 (3)	7046 (3)	−3533 (3)	31 (1)
C12	8959 (4)	8229 (4)	−4612 (3)	44 (2)
C13	9588 (4)	8105 (4)	−5665 (3)	57 (2)
C14	10654 (4)	6824 (4)	−5658 (3)	57 (2)
C15	11115 (4)	5654 (4)	−4599 (3)	55 (2)
C16	10494 (3)	5746 (3)	−3532 (3)	41 (2)
C17	6929 (3)	8768 (3)	−2561 (2)	30 (1)
C18	5918 (3)	8700 (4)	−3126 (3)	45 (2)
C19	4565 (4)	9829 (4)	−3458 (3)	55 (2)
C20	4198 (4)	11018 (4)	−3209 (3)	54 (2)
C21	5165 (4)	11097 (3)	−2622 (3)	48 (2)
C22	6534 (3)	9981 (3)	−2311 (3)	38 (1)
Cl1	7945 (1)	6799 (1)	671 (1)	37 (1)
C3	8329 (4)	4379 (4)	−1580 (3)	43 (2)
P2	8378 (1)	3318 (1)	1149 (1)	26 (1)
C31	7259 (3)	3534 (3)	2428 (3)	31 (1)
C32	6038 (3)	4803 (3)	2262 (3)	42 (2)
C33	5082 (4)	4928 (4)	3183 (3)	54 (2)
C34	5346 (4)	3809 (4)	4254 (3)	57 (2)
C35	6560 (4)	2546 (4)	4443 (3)	57 (2)
C36	7513 (4)	2405 (3)	3530 (3)	43 (2)
C37	7802 (3)	2118 (3)	885 (2)	29 (1)
C38	8707 (3)	731 (3)	971 (3)	39 (2)
C39	8174 (4)	−98 (4)	758 (3)	46 (2)
C40	6760 (4)	448 (4)	435 (3)	44 (2)
C41	5849 (4)	1813 (4)	350 (3)	46 (2)
C42	6364 (3)	2644 (3)	579 (3)	41 (2)
C2	10234 (3)	2093 (3)	1734 (2)	28 (1)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values in this column, the equivalent isotropic U is defined as $^1/_3$ of the trace of the U_{ij} tensor.

Table III. Bond Lengths (Å)^a and Angles (deg) for **3**

	Bond Lengths		
Pd1–P1	2.314 (1)	Pd1–Cl1	2.427 (1)
Pd1–C3	2.056 (5)	Pd1–P2	2.329 (1)
P1–C11	1.834 (3)	P1–C17	1.826 (2)
P1–C2a	1.834 (4)	C11–C12	1.392 (4)
C11–C16	1.391 (4)	C12–C13	1.382 (5)
C13–C14	1.365 (5)	C14–C15	1.372 (4)
C15–C16	1.386 (5)	C17–C18	1.383 (6)
C17–C22	1.381 (5)	C18–C19	1.383 (4)
C19–C20	1.361 (7)	C20–C21	1.369 (7)
C21–C22	1.387 (4)	P2–C31	1.828 (3)
P2–C37	1.836 (4)	P2–C2	1.837 (3)
C31–C32	1.382 (4)	C31–C36	1.383 (4)
C32–C33	1.387 (5)	C33–C34	1.355 (5)
C34–C35	1.372 (5)	C35–C36	1.381 (5)
C37–C38	1.381 (4)	C37–C42	1.383 (5)
C38–C39	1.384 (7)	C39–C40	1.362 (5)
C40–C41	1.363 (5)	C41–C42	1.384 (7)
C2–P1a	1.834 (4)		
	Bond Angles		
P1–Pd1–Cl1	86.9	P1–Pd1–C3	90.7 (1)
Cl1–Pd1–C3	168.7 (1)	P1–Pd1–P2	173.3
Cl1–Pd1–P2	95.3	C3–Pd1–P2	88.4 (1)
Pd1–P1–C11	123.8 (1)	Pd1–P1–C17	110.0 (1)
C11–P1–C17	103.1 (1)	Pd1–P1–C2a	112.1 (1)
C11–P1–C2a	103.0 (2)	C17–P1–C2a	102.6 (2)
P1–C11–C12	121.3 (2)	P1–C11–C16	119.6 (2)
C12–C11–C16	119.0 (3)	C11–C12–C13	120.2 (3)
C12–C13–C14	120.4 (3)	C13–C14–C15	119.9 (4)
C14–C15–C16	120.8 (3)	C11–C16–C15	119.5 (3)
P1–C17–C18	117.8 (3)	P1–C17–C22	124.1 (3)
C18–C17–C22	118.0 (3)	C17–C18–C19	120.9 (4)
C18–C19–C20	120.3 (4)	C19–C20–C21	120.0 (3)
C20–C21–C22	119.9 (4)	C17–C22–C21	120.9 (4)
Pd1–P2–C31	119.9 (1)	Pd1–P2–C37	117.7 (1)
C31–P2–C37	98.8 (2)	Pd1–P2–C2	109.9 (1)
C31–P2–C2	106.9 (1)	C37–P2–C2	101.6 (1)
P2–C31–C32	119.2 (2)	P2–C31–C36	121.6 (2)
C32–C31–C36	118.8 (3)	C31–C32–C33	120.3 (3)
C32–C33–C34	120.1 (3)	C33–C34–C35	120.6 (4)
C34–C35–C36	119.8 (3)	C31–C36–C35	120.4 (3)
P2–C37–C38	124.4 (3)	P2–C37–C42	117.5 (2)
C38–C37–C42	118.1 (4)	C37–C38–C39	120.4 (3)
C38–C39–C40	120.7 (3)	C39–C40–C41	119.7 (5)
C40–C41–C42	120.1 (3)	C37–C42–C41	121.0 (3)
P2–C2–P1a	119.2 (2)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

molecular sieve column. Trimethylaluminum was purchased from Texas-Alkyls and used as received. Perdeuteriotrimethylaluminum was prepared by a literature method.[22] Sodium tetraphenylborate was purchased from Alfa and used as received.

$Pd_2CH_3(Cl)dppm_2$ (2). To a solution of 40 mg (0.04 mmol) of $Pd_2Cl_2dppm_2$[21] (**1**) in 2.5 mL of CD_2Cl_2 at −78 °C was added 50 mL (0.04 mmol) of an 0.80 M trimethylaluminum/methylene chloride solution: ^{1}H NMR (CD_2Cl_2, −78 °C) δ 0.20 (t, 5 Hz, 3 H), 4.04 (m, 4 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −78 °C) 17.71 and 9.87 (AA′BB′, $J_{AA'}$ = 403 Hz, J_{AB} = 79 Hz, $J_{AB'}$ = 12 Hz, $J_{BB'}$ = 325 Hz).

$Pd_2(CH_3)_2(Cl)_2dppm_2$ (3). When the solution of $Pd_2CH_3(Cl)dppm_2$ (**2**) was warmed to ambient temperature, disproportionation to $Pd_2(CH_3)_2Cl_2dppm_2$ (**3**) and **4** took place after filtration of some precipitated **5**; 32.5 mg (75%) of **3** crystallized from solution: [^{1}H NMR (CD_2Cl_2) δ 3.89 (s, br d, 4 H), 0.63 (qi, J = 3.0 Hz, 6 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 17.3 (s). Anal. Calcd for $C_{52}H_{50}Cl_2P_4Pd_4$: C, 57.69; H, 4.66. Found: C, 57.41; H, 4.57. Crystals suitable for X-ray were obtained by vapor diffusion of diethyl ether into a nitromethane solution of **3**.

Complex **4** could be observed in solution: ^{1}H NMR (CD_2Cl_2) δ 4.00 (m, b); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 22 (s).

Structure Determination for 3. Crystal data for **3**, together with details of the X-ray diffraction experiment and subsequent calculations, are

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(22) (a) Pasynkiewicz, S.; Boleslawski, M. *J. Organomet. Chem.* **1970**, *25*, 29. (b) Yang, P. H.; Liou, K. F.; Lin, Y.-T. *J. Organomet. Chem.* **1986**, *307*, 273.

given in Table I. The unit cell dimensions were obtained from a least-squares fit to the setting angles of 24 reflections (2θ(av) = 18.6°).[23] The intensities of three reflections (2 0 −1, −4 −6 −2, 2 1 −5) were measured every 97 reflections. No significant change in the intensities of these reflections was noted during data collection. No absorption correction was performed, due to the low value of the absorption coefficient (range of transmission factors ±2% about the mean value). Lorentz and polarization corrections were applied to the data.

The structure was solved by using the direct methods routine SOLV.[23] In the final structural model, all non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were included in idealized positions (C–H = 0.96 Å, $U_H = 1.2U_{iso}(C)$). At convergence (weighted-least-squares refinement on F, (shift/esd)av <0.016 over the last three cycles) the final ΔF map exhibited a maximum of 0.43 e Å^{-3} (in the immediate vicinity of Pd1) and a minimum of −0.32 e Å^{-3}.

Final fractional atomic coordinates for all non-hydrogen atoms of **3** are listed in Table II, and bond lengths and angles for **3** are listed in Table III.

$Pd_2(\mu-CH_2)Cl_2(dppm)_2$ (5). A solution of **2** in methylene chloride was allowed to warm to ambient temperature. The solution turned red and some product (**5**) precipitated from solution and was removed by filtration. When the reaction was carried out in CD_2Cl_2, the formation of **5**[10b] was accompanied by the disappearance of **4**: ^1H NMR (CD_2Cl_2) δ 3.58 (d of qd, J_{H-H} = 14.0 Hz, J_{P-H} = 4.71 Hz, 2 H), 2.82 (d of qu, J_{H-H} = 14.0 Hz, J_{P-H} = 3.3 Hz, 2 H), 1.66 (qi, J_{P-H} = 8.0 Hz, 2 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 15.1 (s).

$[Pd_2(\mu-Cl)H(CH_3)dppm_2]BPh_4$ (6-H). To a rapidly stirred solution of 1.35 g (1.28 mmol) of $Pd_2Cl_2dppm_2$ (**1**) in 25 mL of CH_2Cl_2 at −78 °C a solution of 0.18 g (2.57 mmol) of trimethylaluminum in 5 mL of methylene chloride was added over 20 min. The initially dark red solution turned dark yellow. After stirring for 10 min, a solution of 0.44 g (1.28 mmol) of sodium tetraphenylborate in 20 mL of ethanol was added over a 20-min period at −78 °C, whereupon the solution turned bright yellow. The volume of the solution was reduced to ~5 mL at high vacuum at −78 °C. Approximately 20 mL of ethanol and 10 mL of diethyl ether precooled to −78 °C were then added, and the solution was filtered at −78 °C. The resulting light yellow precipitate was washed with 3 × 10 mL of diethyl ether, leaving 1.44 g (83%) of a light yellow powder: ^1H NMR (CD_2Cl_2) δ 3.91 (qi, J_{P-H} = 4.0 Hz, 4 H), 0.65 (t, J = 6.0 Hz, 3 H), −12.42 (t, J = 10.0 Hz, 1 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.79, 16.27 (AA′BB′, $J_{AA'}J_{BB'}$ = 9 Hz, J_{AB} = 50 Hz, $J_{AB'}$ = 3 Hz); IR (Nujol) 2050 (w) cm^{-1}; m/z $Pd_2P_4C_{52}H_{51}^+$, 1011. Anal. Calcd for $C_{75}H_{68}BClP_4Pd_2$: C, 66.61; H, 5.07; Cl, 2.62; P, 9.16. Found: C, 66.53; H, 4.93; Cl, 2.77; P, 4.37.

Crystals suitable for X-ray diffraction studies were obtained from CH_2Cl_2. When this reaction was carried out by using perdeuteriotrimethylaluminum,[22] complex **6-D** was obtained.

Structure Determination for 6. Crystal data for **6**, together with details of the X-ray diffraction experiment and subsequent calculations, are given in Table I. The unit cell dimensions were obtained from a least-squares fit to the setting angles of 25 reflections (2θ(av) = 20.46°). The intensities of three reflections (4 3 −2, 1 −7 0, −3 −2 −5) were measured every 97 reflections. No significant change in the intensities of these reflections was noted during data collection. No absorption correction was performed, due to the low value of the absorption coefficient (range of transmission factor ±3% about the mean value). Lorentz and polarization corrections were applied to the data.

Analysis of the Patterson map established the positions of the two palladium atoms. Subsequent difference electron density maps revealed all non-hydrogen ligand atoms and the atoms of three occluded methylene chloride molecules. In the final structural model, all non-hydrogen atoms of the palladium dimer and the counterion were given anisotropic thermal parameters. Hydrogen atoms bound to carbon were included as in the structural model for **3**. The hydride atom, H1, was located, and its position was refined. Two of the three occluded solvent molecules were highly disordered; site occupancy factors were refined for atoms of these molecules. At convergence (weighted-least-squares refinement on F, (shift/esd)av < 0.30 over the last eight cycles) the final ΔF map exhibited a maximum of 1.26 e Å^{-3} (in the immediate vicinity of C17) and a minimum of −0.35 e Å^{-3}.

Final fractional atomic coordinates for all non-hydrogen atoms of **6** are listed in Table IV, and bond lengths and angles for **6** are listed in Table V.

$Pd_2(CH_3)_2dppm_2$ (7). To a solution of 50 mg (4.7 × 10^{-5} mol) of $Pd_2Cl_2dppm_2$ (**1**) in 3 mL of methylene chloride at −78 °C was added a solution of 68 mg (9.5 × 10^{-4} mol) of trimethylaluminum in 1 mL of CD_2Cl_2. The solution was warmed to −40 °C, and after stirring for 3 h the solution was cannulated into a NMR tube, and the product was analyzed by $^{31}P\{^1H\}$ and ^1H NMR at −30 °C: ^1H NMR (CD_2Cl_2, −30 °C) δ 4.01 (br, 4 H), 0.45 (s, 6 H); $^{31}P\{^1H\}$ NMR δ 19.45 (s).

$[Pd_2(\mu-H)(CH_3)_2dppm_2]BPh_4$ (8-H). To a rapidly stirred solution of 371 mg (0.352 mmol) of $Pd_2Cl_2dppm_2$ in 15 mL of CH_2Cl_2 at −78 °C was added a solution of 508 mg (7.04 mmol) of trimethylaluminum in 5 mL of methylene chloride over a 20-min period. The initially dark red solution turned very dark green. The solution was warmed slowly to −40 °C and stirred for 3 h. A solution of 121 mg (0.352 mmol) of sodium tetraphenylborate in 10 mL of ethanol was added over a 20-min period, whereupon the solution turned light yellow. The volume of the solution was reduced to 5 mL under high vacuum at −40 °C. Approximately 20 mL of ethanol and 10 mL of diethyl ether was added, and the solution was filtered at −40 °C. The resulting light yellow precipitate was washed with 3 × 10 mL of diethyl ether, leaving 0.328 g (70%) of a light yellow powder: ^1H NMR (CD_2Cl_2) δ 4.57 (q, 3.0 Hz, 4 H), 0.07 (br, 6 H), −7.55 (q, 15.0 Hz, 1 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 22.3 (s); IR (Nujol) 2001 (w) cm^{-1}. Anal. Calcd for $C_{76}H_{71}BP_4Pd_2$: C, 68.53; H, 5.38. Found: C, 68.49; H, 5.31.

When this reaction was carried out with perdeuteriotrimethylaluminum, complex **8-D** was obtained. Crystals of **8-H** suitable for X-ray diffraction studies could be obtained from CH_2Cl_2 by slow evaporation of the solvent. However, the solution and refinement of the structure confirmed that some chloride was introduced into **8-H** (μ-Cl for μ-H) by this technique, and the structure determination confirmed that these structurally similar species had cocrystallized. Refinement of the site occupancy factor for the single bridging atom seen (modeled as a chlorine atom) indicated that approximately 15% of the hydride sites were occupied by chloride ions in the data collection crystal. No further refinement of this structure was carried out.

Thermolysis of 6-H and 8-H. The decompositions of **6-H** and **8-H** were carried out by warming methylene chloride solutions of the complexes and observing the reaction by ^1H and ^{31}P NMR to obtain the approximate temperatures at which decomposition took place. The organic reaction products were analyzed by GC/mass spectrometry. The amount of methane or ethane was obtained by carrying out the decomposition on a vacuum line and measuring the volume of noncondensable gas (Toepler pump).

Typically, a 5-mL solution of **6-H** (21 mg, 1.5 × 10^{-2} mmol) in methylene chloride was warmed to ambient temperature for 7 h. When a solution of **6-H** as its chloride salt (obtained from **2** without having added sodium tetraphenyl borate) was warmed to −20 °C, decomposition and the quantitative elimination of methane took place. When the reaction was complete, evaporation of the solution and washing out the aluminum salts gave an 80% yield of **1**. The same result could be obtained by adding lithium chloride to an acetone solution of the tetraphenylborate salt of **6-H**. In this case, **1** crystallized from solution at 0 °C. Thermolysis of the tetraphenylborate salt of **6-H** in methylene chloride took place at 23 °C for 17 h to give a quantitative yield of methane and 33% yields of both the face-to-face dimer **3** and **1**.

Thermolyses of **8-H** were carried out similarly. A 4-mL solution of **8-H** (17 mg, 1.2 × 10^{-2} mmol) in methylene chloride was warmed to 23 °C for 24 h. An ~1:1 mixture of methane and ethane (GC/mass spectrum) was observed, while decomposition of a solution of **8-H** as its chloride salt (obtained from **2** without having added sodium tetraphenylborate) gave methane and ethane in an ~2:1 ratio. Both the face-to-face dimer **3** and the A-frame dimer **5** were isolated as products from decomposition of the chloride salt. Face-to-face dimer **3** and an unidentified palladium complex ($^{31}P\{^1H\}$ NMR δ 19.2) were produced from the tetraphenylborate salt. Crossover experiments with **6-H** and **6-D** or **8-H** and **8-D** were carried out with two 5-mL solutions (1.7 × 10^{-2} mmol) in **6-H** and **6-D** or **8-H** and **8-D** in methylene chloride. Portions of the solutions, 1.5 mL each, of the deuteriated and undeuteriated complexes were withdrawn and mixed to produce the crossover solution. The three solutions were then warmed to ambient temperature for 20 h; and the volatile products were then vacuum transferred and analyzed by GC/mass spectroscopy.

$[Pd_2(\mu-CO)H(CH_3)Cldppm_2]BPh_4$ (10). A flask fitted with a vacuum stopcock and a septum cap was charged with 145 mg (0.107 mmol) of $[Pd_2(\mu-Cl)H(CH_3)dppm_2]BPh_4$ (**6-H**), and 30 mL of methylene chloride was vacuum transferred into the flask. The solution was degassed by three freeze/pump/thaw cycles. Carbon monoxide was bubbled vigorously through the solution which was maintained at −22 °C. After 4 h

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[23] Software used for diffractometer operations and data collection was provided with the Nicolet R3m diffractometer. Crystallographic computations were carried out with the SHELXTL program library, written by G. M. Sheldrick and supplied by Nicolet XRD for the Data General Eclipse S/140 computer in the crystallography laboratory at Colorado State University.

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)[a] for **6**

atom	*x*	*y*	*z*	U_{iso}[b]	atom	*x*	*y*	*z*	U_{iso}[b]
Pd1	4192 (1)	6172 (1)	3046 (1)	17 (1)*	C401	5836 (7)	8560 (5)	3595 (5)	22 (3)*
Pd2	6371 (1)	6671 (1)	3325 (1)	16 (1)*	C402	6517 (7)	9156 (5)	3291 (5)	24 (3)*
P1	3168 (2)	7466 (1)	2846 (1)	19 (1)*	C403	6791 (8)	9568 (6)	3763 (6)	33 (4)*
P2	5475 (2)	4963 (1)	3006 (1)	18 (1)*	C404	6428 (9)	9392 (6)	4527 (6)	35 (4)*
P3	7438 (2)	5409 (1)	3610 (1)	18 (1)*	C405	5768 (9)	8803 (6)	4832 (6)	35 (4)*
P4	5478 (2)	7964 (1)	3012 (1)	16 (1)*	C406	5480 (8)	8372 (5)	4377 (5)	28 (3)*
Cl1	4643 (2)	6333 (1)	4260 (1)	21 (1)*	C407	5815 (7)	8476 (5)	2053 (5)	19 (3)*
C1	3467 (8)	5917 (5)	2232 (5)	25 (3)*	C408	6712 (7)	8126 (5)	1537 (5)	25 (3)*
C2	3829 (7)	8093 (5)	3254 (5)	19 (3)*	C409	6965 (8)	8522 (6)	801 (5)	32 (4)*
C3	6456 (7)	4694 (5)	3716 (5)	19 (3)*	C410	6323 (8)	9245 (6)	575 (5)	29 (3)*
C101	1566 (7)	7620 (5)	3268 (5)	23 (3)*	C411	5408 (8)	9611 (5)	1095 (5)	29 (2)
C102	1139 (8)	7846 (6)	3957 (6)	35 (4)*	C412	5162 (8)	9224 (5)	1834 (5)	26 (2)
C103	−93 (9)	7934 (6)	4255 (6)	42 (4)*	B1	469 (9)	1091 (6)	2547 (6)	27 (2)
C104	−894 (8)	7787 (6)	3889 (7)	41 (4)*	C501	1330 (8)	1653 (5)	1950 (5)	24 (2)
C105	−470 (9)	7534 (6)	3205 (6)	40 (4)*	C506	2410 (8)	1319 (5)	1503 (5)	25 (2)
C107	3147 (7)	7982 (5)	1880 (4)	18 (3)*	C505	3147 (9)	1776 (5)	971 (5)	31 (2)
C108	3947 (8)	7680 (5)	1280 (5)	27 (3)*	C504	2821 (9)	2587 (6)	836 (6)	38 (2)
C109	3922 (9)	8094 (6)	550 (5)	33 (4)*	C503	1751 (10)	2935 (7)	1247 (6)	42 (3)
C110	3137 (8)	8802 (6)	431 (5)	32 (4)*	C502	1020 (9)	2472 (5)	1800 (5)	30 (2)
C111	2365 (8)	9114 (5)	1025 (5)	27 (3)*	C507	−675 (8)	1621 (5)	3038 (5)	26 (2)
C112	2370 (8)	8710 (5)	1749 (5)	25 (3)*	C508	−490 (9)	1996 (6)	3577 (5)	33 (2)
C106	741 (8)	7459 (6)	2894 (6)	35 (4)*	C509	−1388 (9)	2386 (6)	4058 (6)	36 (2)
C201	4773 (7)	4109 (5)	3135 (5)	21 (3)*	C510	−2571 (10)	2450 (6)	3977 (6)	43 (3)
C202	4603 (8)	3849 (5)	2511 (5)	29 (3)*	C511	−2824 (11)	2125 (7)	3455 (7)	53 (3)
C203	4001 (9)	3228 (6)	2620 (6)	39 (4)*	C512	−1902 (10)	1700 (7)	2993 (6)	44 (3)
C204	3574 (8)	2863 (5)	3344 (6)	37 (4)*	C513	1209 (8)	493 (5)	3176 (5)	23 (2)
C205	3724 (8)	3124 (5)	3957 (6)	35 (4)*	C514	602 (9)	34 (5)	3799 (5)	30 (2)
C206	4341 (8)	3743 (5)	3853 (5)	26 (3)*	C515	1159 (8)	−434 (5)	4385 (5)	30 (2)
C207	6585 (8)	4944 (5)	2141 (5)	26 (3)*	C516	2384 (8)	−461 (5)	4381 (5)	30 (2)
C208	7375 (9)	4245 (6)	2001 (6)	35 (4)*	C517	3014 (8)	−14 (5)	3784 (5)	27 (2)
C209	8269 (10)	4247 (7)	1377 (6)	51 (5)*	C518	2442 (8)	447 (5)	3197 (5)	27 (2)
C210	8377 (11)	4925 (9)	896 (7)	69 (6)*	C519	−56 (8)	613 (5)	2043 (5)	26 (2)
C211	7613 (10)	5638 (8)	1020 (6)	55 (5)*	C520	−405 (8)	−127 (5)	2308 (5)	31 (2)
C212	6720 (9)	5649 (7)	1636 (5)	37 (4)*	C521	−848 (9)	−490 (6)	1844 (5)	36 (2)
C301	8855 (7)	5050 (5)	3016 (5)	18 (3)*	C522	−974 (9)	−137 (6)	1126 (6)	37 (2)
C302	9452 (8)	4276 (5)	3181 (5)	27 (3)*	C523	−641 (9)	589 (6)	852 (6)	39 (2)
C303	10587 (8)	4022 (6)	2780 (6)	32 (4)*	C524	−203 (8)	952 (6)	1295 (5)	31 (2)
C304	11151 (9)	4540 (6)	2230 (6)	36 (4)*	Cl2	5314 (4)	1158 (3)	2538 (2)	85 (1)
C305	10569 (9)	5311 (6)	2058 (6)	40 (4)*	C10	6237 (12)	1323 (8)	1705 (7)	62 (3)
C306	9415 (8)	5572 (6)	2440 (5)	31 (3)*	Cl3	6438 (4)	2236 (3)	1318 (3)	99 (1)
C307	7895 (7)	5239 (5)	4521 (4)	18 (3)*	Cl4	2292 (7)	6459 (4)	303 (4)	161 (3)
C308	8341 (8)	5839 (5)	4689 (5)	23 (3)*	C11	1188 (19)	7369 (12)	219 (12)	115 (7)
C309	8757 (8)	5729 (5)	5359 (5)	26 (3)*	Cl5	143 (8)	7542 (5)	951 (5)	180 (3)
C310	8706 (8)	5025 (5)	5872 (5)	26 (3)*	Cl6	4130 (8)	4539 (5)	463 (5)	187 (3)
C311	8277 (8)	4442 (5)	5699 (5)	26 (3)*	C12	5382 (47)	5212 (28)	372 (27)	297 (24)
C312	7881 (7)	4536 (5)	5029 (5)	24 (3)*	Cl7	3999 (22)	6783 (14)	−747 (14)	526

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic *U* is defined as $^1/_3$ of the trace of the U_{ij} tensor.

a precipitate formed, and the solution was cooled to −78 °C and filtered. The resulting solid was washed with 3 × 10 mL of cold ether (−78 °C). A slurry of the solid in CH_2Cl_2 at −78 °C was charged to a solution IR cell, and the spectrum was recorded: IR (CH_2Cl_2, <−20 °C) 1695 cm^{-1}; ^{1}H NMR (CD_2Cl_2, −20 °C) δ 4.1 (m, 4 H), 1.0 (m, 3 H), −11.3 (br, 1 H).

[Pd$_2$(μ-Cl)(COCH$_3$)Hdppm$_2$]BPh$_4$ (11). A flask fitted with a vacuum stopcock and septum cap was charged with 152 mg (0.112 mmol) of **6-H** and was degassed by three freeze/pump/thaw cycles. Carbon monoxide was added slowly to the head space (~2.5 cm Hg pressure), while the solution was stirred at −21 °C. After 72 h crystals formed on the side of the flask, and the solution was filtered at −78 °C and washed with 3 × 15 mL of ether, leaving 77 mg (50%) of a light brown powder: ^{1}H NMR (CD_2Cl_2, −20 °C) δ 4.08 (m, 4 H), 1.72 (s, 3 H), −10.02 (br, 1 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −20 °C) δ 23.5, 7.8 (AA′BB′, $J_{AA'}J_{BB'}$ = 10 Hz, J_{AB} = 52 Hz, $J_{AB'}$ = 2 Hz); IR (CH_2Cl_2) ν(CO) 1715 cm^{-1}.

This complex was somewhat unstable and attempts to obtain the X-ray structure led to decomposition of the crystals.

When the carbonylation was carried out in acetone in the presence of lithium chloride at −50 °C, a peak in the ^{1}H NMR spectrum at δ 10.20 was observed in the early stages of the reaction.

[Pd$_2$(μ-H)(COCH$_3$)CH$_3$dppm$_2$]BPh$_4$ (12). A flask fitted with a vacuum stopcock and septum cap was charged with 178 mg (0.133 mmol) of **8-H**. To this flask, approximately 30 mL of methylene chloride was vacuum transferred. The solution was degassed with three freeze/pump/thaw cycles. Carbon monoxide was added slowly to the head space (~2.5 mm Hg pressure), while the solution was stirred at −22 °C. After 20 min the initially light yellow solution became red. The NMR analysis of an aliquot of the solution after 30 min revealed the formation of approximately 20% of the palladium monoacyl complex along with unreacted **8-H**: ^{1}H NMR (CD_2Cl_2, −20 °C) δ 4.50 (m, 4 H), 1.64 (s, 3 H), 0.15 (br, 3 H), −7.50 (br, 1 H); IR(CH_2Cl_2) 1701 (s) cm^{-1}.

[Pd$_2$(μ-H)(COCH$_3$)$_2$dppm$_2$]BPh$_4$ (13). The above solution was allowed to react with CO for a total of 48 h, during which the solution turned dark red. The volume of the solvent was reduced to 5 mL, and *n*-hexane (−20 °C) was added. The resulting brown precipitate was filtered and washed with 3 × 5 mL of cold ether to yield 127 mg (69%) of product: ^{1}H NMR (CD_2Cl_2, −20 °C) δ 4.46 (m, 4 H), 1.68 (s, 6 H), −7.55 (br, 1 H); $^{31}P\{^1H\}$ NMR δ 18.26 (s); IR (CH_2Cl_2) ν(CO) 1708 cm^{-1}.

Reductive Elimination of Acetaldehyde from 11 and 13. An NMR tube containing 17 mg (1.3 × 10^{-2} mmol) of **6** was evacuated overnight, and then 2 mL of dry, degassed solvent (CD_2Cl_2 or CD_3COCD_3) was vacuum transferred into the tube at −196 °C. The solution was warmed to −100 °C, and CO was charged to the tube. The series of reactions were observed by warming the sample in the NMR spectrometer. At −22 °C, the insertion of CO took place. Warming the reaction to ambient temperature produced acetaldehyde (GC/mass spectrum), **1**, and Pd$_2$(μ-CO)Cl$_2$dppm$_2$, which was identified by comparison to an authentic sample obtained by the carbonylation of **1**.[19] When CD_3COCD_3 **D-6** acetone was used as the solvent, CO insertion took place at −40 °C, and the reductive elimination was complete at −20 °C. The addition of lithium chloride to a CD_3COCD_3 solution of **6-H** promoted the CO reaction, which took place at −95 °C as the solvent melted.

Approximately 1 mL of perdeuterioacetone was vacuum transferred into a 5-mm NMR tube at −196 °C containing 7 mg of **6-H** and 1 mg

Table V. Bond Lengths (Å)[a] and Angles (deg) for **6**

Bond Lengths

Pd1–P1	2.320 (2)	Pd1–P2	2.313 (2)	C309–C310	1.402 (12)	C310–C311	1.361 (15)
Pd1–Cl1	2.508 (2)	Pd1–C1	2.050 (11)	C311–C312	1.380 (14)	C401–C402	1.403 (13)
Pd2–P3	2.305 (2)	Pd2–P4	2.293 (2)	C401–C406	1.409 (12)	C402–C403	1.381 (16)
Pd2–Cl1	2.427 (2)	P1–C2	1.839 (10)	C403–C404	1.375 (14)	C404–C405	1.378 (15)
P1–C101	1.818 (8)	P1–C107	1.832 (8)	C405–C406	1.385 (17)	C407–C408	1.380 (11)
P2–C3	1.836 (9)	P2–C201	1.819 (9)	C407–C412	1.390 (11)	C408–C409	1.396 (12)
P2–C207	1.820 (8)	P3–C3	1.831 (9)	C409–C410	1.355 (12)	C410–C411	1.404 (12)
P3–C301	1.821 (7)	P3–C307	1.826 (9)	C411–C412	1.396 (12)	B1–C501	1.639 (13)
P4–C2	1.820 (8)	P4–C401	1.827 (11)	B1–C513	1.644 (13)	C501–C506	1.417 (11)
P4–C407	1.817 (8)	C101–C102	1.376 (14)	C501–C502	1.395 (12)	C506–C505	1.395 (12)
C101–C106	1.399 (16)	C102–C103	1.388 (13)	C505–C504	1.382 (14)	C504–C503	1.387 (14)
C103–C104	1.355 (18)	C104–C105	1.388 (16)	C503–C502	1.415 (14)	C507–C508	1.392 (16)
C105–C106	1.372 (13)	C107–C108	1.399 (12)	C507–C512	1.403 (15)	C508–C509	1.371 (13)
C107–C112	1.399 (11)	C108–C109	1.399 (12)	C509–C510	1.375 (16)	C510–C511	1.341 (19)
C109–C110	1.375 (12)	C110–C111	1.387 (13)	C511–C512	1.394 (15)	C513–C514	1.409 (12)
C111–C112	1.382 (12)	C201–C202	1.400 (15)	C513–C518	1.408 (13)	C514–C515	1.399 (13)
C201–C206	1.389 (12)	C202–C203	1.385 (15)	C515–C516	1.394 (14)	C516–C517	1.381 (12)
C203–C204	1.394 (14)	C204–C205	1.373 (18)	C517–C518	1.404 (12)	C519–C520	1.411 (13)
C205–C206	1.394 (14)	C207–C208	1.396 (13)	C519–C524	1.419 (13)	C520–C521	1.413 (17)
C207–C212	1.408 (13)	C208–C209	1.369 (13)	C521–C522	1.369 (14)	C522–C523	1.383 (15)
C209–C210	1.346 (18)	C210–C211	1.398 (19)	C523–C524	1.380 (17)	Cl2–C10	1.684 (13)
C211–C212	1.360 (13)	C301–C302	1.388 (11)	C10–Cl3	1.667 (14)	Cl3–Cl7a	1.854 (22)
C301–C306	1.397 (12)	C302–C303	1.382 (12)	Cl4–C11	1.811 (20)	C11–Cl5	1.639 (21)
C303–C304	1.370 (13)	C304–C305	1.381 (14)	Cl6–C12	2.024 (59)	Cl6–C12a	1.534 (47)
C305–C306	1.387 (12)	C307–C308	1.395 (14)	C12–Cl6a	1.534 (47)	Cl7–Cl3a	1.854 (22)
C307–C312	1.392 (11)	C308–C309	1.389 (14)				

Bond Angles

P1–Pd1–P2	167.8 (1)	P1–Pd1–Cl1	91.2 (1)	P3–C301–C302	120.2 (6)	P3–C301–C306	120.2 (6)
P2–Pd1–Cl1	95.0 (1)	P1–Pd1–C1	90.8 (2)	C302–C301–C306	119.3 (7)	C301–C302–C303	120.6 (8)
P2–Pd1–C1	85.9 (2)	Cl1–Pd1–C1	165.3 (2)	C302–C303–C304	120.1 (8)	C303–C304–C305	120.1 (8)
P3–Pd2–P4	174.8 (1)	P3–Pd2–Cl1	90.1 (1)	C304–C305–C306	120.6 (9)	C301–C306–C305	119.3 (8)
P4–Pd2–Cl1	94.5 (1)	Pd1–P1–C2	110.6 (3)	P3–C307–C308	117.2 (6)	P3–C307–C312	123.5 (8)
Pd1–P1–C101	115.0 (3)	C2–P1–C101	104.9 (4)	C308–C307–C312	119.2 (8)	C307–C308–C309	119.8 (7)
Pd1–P1–C107	118.6 (3)	C2–P1–C107	103.7 (4)	C308–C309–C310	120.1 (9)	C309–C310–C311	119.4 (9)
C101–P1–C107	102.6 (4)	Pd1–P2–C3	113.3 (3)	C310–C311–C312	121.2 (8)	C307–C312–C311	120.2 (9)
Pd1–P2–C201	117.2 (3)	C3–P2–C201	103.9 (4)	P4–C401–C402	122.1 (7)	P4–C401–C406	118.2 (7)
Pd1–P2–C207	113.0 (3)	C3–P2–C207	101.9 (4)	C402–C401–C406	119.6 (10)	C401–C402–C403	119.3 (8)
C201–P2–C207	106.1 (4)	Pd2–P3–C3	110.2 (2)	C402–C403–C404	121.0 (9)	C403–C404–C405	120.1 (11)
Pd2–P3–C301	121.3 (3)	C3–P3–C301	106.3 (4)	C404–C405–C406	120.6 (9)	C401–C406–C405	119.3 (9)
Pd2–P3–C307	111.2 (3)	C3–P3–C307	104.3 (4)	P4–C407–C408	120.4 (6)	P4–C407–C412	120.1 (6)
C301–P3–C307	102.1 (4)	Pd2–P4–C2	111.1 (3)	C408–C407–C412	119.5 (7)	C407–C408–C409	120.1 (7)
Pd2–P4–C401	110.1 (3)	C2–P4–C401	102.8 (4)	C408–C409–C410	121.1 (8)	C409–C410–C411	119.4 (8)
Pd2–P4–C407	119.6 (3)	C2–P4–C407	106.1 (4)	C410–C411–C412	119.8 (8)	C407–C412–C411	120.0 (8)
C401–P4–C407	105.7 (4)	Pd1–C11–Pd2	75.2 (1)	C501–B1–C513	111.9 (8)	B1–C501–C506	120.8 (8)
P1–C2–P4	114.2 (4)	P2–C3–P3	112.1 (4)	B1–C501–C502	123.5 (7)	C506–C501–C502	115.5 (7)
P1–C101–C102	122.9 (8)	P1–C101–C106	118.4 (7)	C501–C506–C505	122.6 (8)	C506–C505–C504	120.7 (8)
C102–C101–C106	118.6 (8)	C101–C102–C103	120.0 (11)	C505–C504–C503	118.4 (9)	C504–C503–C502	120.9 (9)
C102–C103–C104	121.3 (11)	C103–C104–C105	119.2 (9)	C501–C502–C503	121.9 (8)	C508–C507–C512	113.9 (8)
C104–C105–C106	120.2 (11)	P1–C107–C108	120.9 (6)	C507–C508–C509	125.5 (10)	C508–C509–C510	117.6 (11)
P1–C107–C112	119.1 (6)	C108–C107–C112	119.8 (7)	C509–C510–C511	120.5 (10)	C510–C511–C512	121.1 (12)
C107–C108–C109	119.6 (7)	C108–C109–C110	119.7 (8)	C507–C512–C511	121.4 (12)	B1–C513–C514	121.2 (8)
C109–C110–C111	121.0 (8)	C110–C111–C112	120.0 (8)	B1–C513–C518	124.8 (7)	C514–C513–C518	113.7 (8)
C107–C112–C111	119.8 (8)	C101–C106–C105	120.5 (10)	C513–C514–C515	123.9 (9)	C514–C515–C516	120.3 (8)
P2–C201–C202	120.1 (6)	P2–C201–C206	119.8 (8)	C515–C516–C517	117.8 (8)	C516–C517–C518	121.1 (9)
C202–C201–C206	120.0 (9)	C201–C202–C203	119.3 (9)	C513–C518–C517	123.2 (8)	C520–C519–C524	114.9 (10)
C202–C203–C204	120.2 (11)	C203–C204–C205	120.7 (10)	C519–C520–C521	121.1 (9)	C520–C521–C522	121.6 (10)
C204–C205–C206	119.6 (9)	C201–C206–C205	120.2 (10)	C521–C522–C523	118.6 (11)	C522–C523–C524	120.6 (10)
P2–C207–C208	120.6 (7)	P2–C207–C212	119.9 (7)	C519–C524–C523	123.1 (9)	Cl2–C10–Cl3	120.0 (8)
C208–C207–C212	119.3 (8)	C207–C208–C209	120.3 (9)	C10–Cl3–Cl7a	152.7 (11)	Cl4–C11–Cl5	118.2 (12)
C208–C209–C210	119.7 (11)	C209–C210–C211	121.8 (10)	C12–Cl6–C12a	72.0 (32)	Cl6–C12–Cl6a	108.0 (32)
C210–C211–C212	119.4 (11)	C207–C212–C211	119.5 (10)				

[a] Estimated standard deviations in the least significant digits are given in parentheses.

of LiCl. Carbon monoxide was charged to the tube, which was allowed to warm to −80 °C. At −75 °C, **6-H** was completely consumed. At −60 °C, a 1:1:2 mixture of $Pd_2Cl_2(COCH_3)H(dppm)_2$ (**11**), $Pd_2Cl_2(CHO)CH_3dppm$ (**12**), and $Pd_2Cl_2dppm_2$ (**1**) appeared. By the time the temperature reached −50 °C the reductive elimination of acetaldehyde was complete.

When a 5-mL solution of **11** (20 mg, 1.4 × 10^{-2} mmol) in methylene chloride was warmed to 23 °C for 48 h, acetaldehyde was evolved, and three palladium species were formed in solution, as observed by ^1H NMR: **1** (14%), the face-to-face dimer **3** (24%), and an unidentified product (^{31}P NMR at δ −7.9 ppm).

The thermal decomposition reaction of a 5-mL solution of **13** (15 mg, 1 × 10^{-2} mmol) in methylene chloride, on warming to 23 °C for 24 h, produced acetaldehyde and chloroacetone but no biacetyl (GC/mass spectrum) as well as the face-to-face dimer (32%).

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115305-72-1; **5**, 78274-94-9; **6-H**·$2CH_2Cl_2$, 115290-48-7; **7**, 115290-49-8; **8-D**, 115290-52-3; **8-H**, 115290-50-1; **8-H** (Cl salt), 115290-61-4; **10**, 115290-54-5; **11**, 115290-56-7; **12**, 115290-58-9; **13**, 115290-60-3; Me_3Al, 75-24-1; CH_4, 74-82-8; CH_3CH_3, 74-84-0; CH_3CO, 75-07-0; perdeuteriotrimethylaluminum, 5630-35-3.

Supplementary Material Available: Table S-I, anisotropic thermal parameters for **3**; Table S-II, calculated hydrogen atom positions for **3**; Table S-III, anisotropic thermal parameters for **6**; Table S-IV, calculated hydrogen atom positions for **6** (10 pages); Tables S-V and S-VI, calculated and observed structure factors for **3** and **6**, respectively (92 pages). Ordering information is given on any current masthead page.

Intramolecular Long-Range Electron Transfer in the α-Hemoglobin Subunit

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Abstract: The single sulfhydryl group (Cys-104) of the isolated human α-hemoglobin chain was converted to a mixed disulfide with 5,5′-dithiobis(2-nitrobenzoic acid). The mixed disulfide on the protein can be reduced to its radical anion with the pulse radiolytically generated formate radical, $CO_2^{\bullet-}$. The electron of the disulfide radical anion then transfers to the protein heme group at a nominal distance of approximately 12 Å with an intramolecular rate constant of 188 ± 23 s^{-1} at room temperature and pH 7. The disulfide radical anions formed from 5,5′-dithiobis(2-nitrobenzoic acid) and from the mixed disulfide on the protein have similar E_{m7}, −42 ± 1 and −41 ± 1 mV, respectively.

It is now apparent that intramolecular electron transfer can occur over relatively long distances in proteins (Table II and ref 2–7). While a number of factors may affect such long-range electron transfers (LRET)[1]—among them the distance, geometric disposition and redox potential between donor, and acceptor and the solvent/structural reorganization accompanying the transfer[8]—there is insufficient data to assess the relative importance of any one factor for LRET in proteins. Since LRET may play an important role in (i) physiologically significant electron-transfer reactions, (ii) damage of proteins and nucleic acids by ionizing radiation, and (iii) the potentially destructive reactions of metabolically generated free radicals, it is important to explore the mechanism(s) of LRET in biological macromolecules. Most protein LRET studies have involved electron transfer between metal centers held apart, at presumably fixed distances. There are fewer examples with an organic free radical as the electron donor and/or acceptor. Prütz and co-workers[9] reported that the tryptophan radical oxidizes tyrosine within the same peptide or protein, and we[10] have shown that the disulfide bond(s) of RNase A can be reduced to the disulfide radical anion ($RSSR^{\bullet-}$) in an intramolecular process. In this paper we report that the organic radical $RSSR^{\bullet-}$, formed by formate radical ($CO_2^{\bullet-}$) reduction of a mixed disulfide (eq 1) attached to cysteine-104 of the isolated α-hemoglobin subunit, can be an electron donor to the heme group in an intramolecular electron transfer (eq 2) over approximately 12 Å.[11]

$$CO_2^{\bullet-} + Fe(III)\text{-}\alpha\text{-Hb-SSR} \rightarrow CO_2 + Fe(III)\text{-}\alpha\text{-Hb-SSR}^{\bullet-} \quad (1)$$

$$Fe(III)\text{-}\alpha\text{-Hb-SSR}^{\bullet-} \rightarrow Fe(II)\text{-}\alpha\text{-Hb-SSR} \quad (2)$$

Experimental Methods and Materials

We treated (carbon monoxy)hemoglobin A, isolated from freshly drawn human blood by the procedure of Uchida and co-workers,[12] with *p*-mercuribenzoate[13] and separated the α-hemoglobin subunit with the following procedure suggested by Alpert. The treated protein was absorbed to a carboxymethyl-cellulose (Whatman C-52) column (1.5 × 30 cm), washed with 10 mM phosphate, pH 7.0, to remove the β-chain, and washed again with 1 mM mercaptoethanol and 1 mM phosphate buffer, pH 7.0, to remove the mercurial. We then eluted the still-adsorbed α-Hb-CO from the resin with a 40 mM Tris, pH 8.0, buffer, dialyzed the eluate against 5 mM phosphate, pH 7.0, and stored it at 4 °C. On the day just before its use, we oxidized the protein for 20 min at 4 °C with a 2-fold molar excess of ferricyanide and then removed ferri- and ferrocyanide with a Dowex 1X-8 column (1 × 5 cm).[12] We next incubated the Fe(III)-α-Hb with a 2-fold excess of DTNB at 4 °C for 1 h, removed the small ligands by dialysis against 5 mM phosphate, 1 M

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(1) Abbreviations used are the following: $CO_2^{\bullet-}$, the formate radical; DTNB, 5,5′-dithiobis(2-nitrobenzoic acid); e_{aq}^-, the hydrated electron; $H^{\bullet}$, the hydrogen atom; LRET, long-range electron transfer; $OH^{\bullet}$, the hydroxyl radical; RNase, pancreatic ribonuclease A; $RSSR^{\bullet-}$, the disulfide radical anion; α-Hb, the isolated α-subunit of human hemoglobin A; Fe(III)-α-Hb-SSR, the mixed-disulfide derivative of oxidized α-Hb formed by the reaction of the subunit with DTNB; Fe(III)-α-Hb-$SSR^{\bullet-}$, the disulfide radical anion form of oxidized Fe(III)-α-Hb-SSR; Fe(II)-α-Hb-SSR, reduced deoxy-α-Hb-SSR.

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(11) Ladner, R. C.; Heidner, E. G.; Perutz, M. F. *J. Mol. Biol.* **1977**, *114*, 385. There is no single value to assign the cysteine sulfur to heme distance. In the crystal structure the center of the sulfur is 13.5 Å from the heme iron, while it is 10.6 Å, the shortest distance to the porphyrin group, from the heme C2C atom. When we simply rotate around the α-C and β-C bond, the minimum and maximum distances between sulfur and heme iron are 11.0 and 13.9 Å, while between sulfur and porphyrin ring they are 8.5 and 11.7 Å. For these minimum distances, however, the disulfide group would have to point directly into the protein interior, and, therefore, the larger distances with the aromatic ring pointing out from the protein would be more reasonable.

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