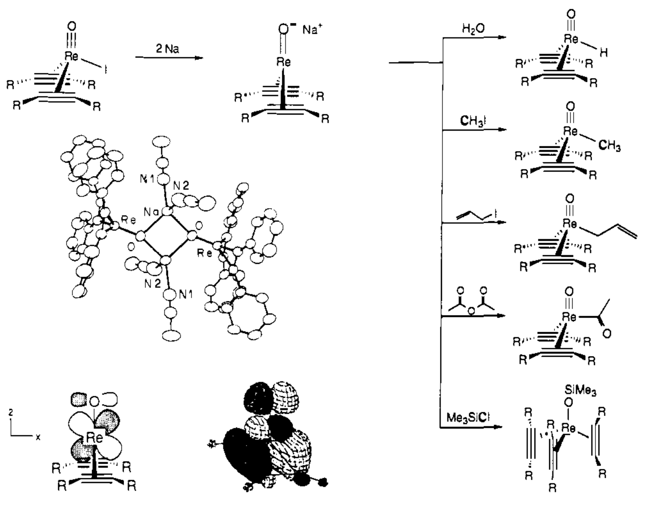
Scheme I



solution, NMR spectra of complexes 2[10] indicate a more symmetrical C_{2v} structure and suggest that acetylene rotation is not facile (the methylene hydrogens in **2b** are diastereotopic).

The rhenium-oxo distance of 1.756 (3) Å is indicative of substantial multiple bonding, but it is one of the longest reported for rhenium monooxo complexes[13,14] (compare 1.70 ± 0.02 Å in six $\mathrm{Re(O)X(MeC{\equiv}CMe)_2}$ structures[7,12]). The Re–O distance in **2c**·2MeCN is more comparable to an Re–O double bond distance (average 1.76 Å in *trans*-$\mathrm{ReO_2}$ species) than the Re–O triple bond present in most rhenium monooxo compounds (average 1.69 Å).[14] The Re–O stretching frequencies in **2a–c** are much lower than in the Re(III) analogues, for instance, 824 cm^{-1} in **2c** (ν(Re–^{18}O) = 763 cm^{-1}) vs 972 cm^{-1} in **1c**. In the presence of 15-crown-5, ν(Re–O) is 885 cm^{-1}, indicating that only part of the large shift is due to the Na–O interaction.

The bond length and low stretching frequencies suggest that Re–O bonding in **2** is weaker than that in **1**. Preliminary calculations[15] indicate that this is due to the population of a Re–O antibonding orbital: the two added electrons occupy the d_{xz} orbital in the mirror plane of the molecule (see drawings in Scheme I) which is Re–O π^* and rhenium–acetylene π backbonding. High electron density in this orbital is consistent with the location of the Na$^+$ ions in the xz plane in the crystal structure. Strong backbonding to the acetylenes is indicated by the short Re–C distances (average 2.006 (5) Å compared to 2.051 (5) Å for the Re-2-butyne distances in **1a**), the long C$\equiv$C distances (average 1.316 (7) Å),[16] and the low C$\equiv$C stretching frequencies (1685 cm^{-1} in **2a** vs 1800 cm^{-1} in **1a**). The presence of significant backbonding complicates the oxidation state assignment: **2a–c** can also be considered as Re(III) if the added electrons are taken to be on the acetylenes rather than the metal, although **2a–c** are nucleophilic at the metal, not at the acetylene ligands.

Compounds **2** are readily protonated (with water), alkylated (with methyl or allyl iodide), and acylated (with acetic anhydride) to form rhenium hydride, methyl, allyl,[12c] and acyl complexes[12d] (Scheme I). The high nucleophilicity of the rhenium center is unprecedented for metal-oxo complexes.[17] Reaction with $\mathrm{Me_3SiCl}$, however, forms a siloxide complex; in the presence of added acetylene, $\mathrm{Re(OSiMe_3)(RC{\equiv}CR)_3}$ is obtained in 30–40% yield. Compounds **2** are rapidly oxidized by atmospheric oxygen or $\mathrm{Cp_2FeBF_4}$ to give $\mathrm{Re_2O_2(RC{\equiv}CR)_4}$ dimers.[9] Further studies are in progress to explore the properties and reactivity of compounds **2**, rare examples of terminal oxo complexes in which metal–oxygen antibonding orbitals are populated.

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Registry No. 1a, 90623-35-1; **1b**, 98778-24-6; **1c**, 123170-29-6; **2a**, 123170-30-9; **2b**, 123170-31-0; **2c**, 123170-32-1; **2c**·$\mathrm{2CD_3CN}$, 123170-35-4; **12a**, 123170-36-5; $\mathrm{Re(OSiMe_3)(EtC{\equiv}CEt)_3}$, 123170-37-6; $\mathrm{EtC{\equiv}CEt}$, 928-49-4.

Supplementary Material Available: Preparations and spectroscopic and analytical data for **2a–c**, $\mathrm{Re(O)[C(O)Me](MeC{\equiv}CMe)_2}$, and $\mathrm{Re(OSiMe_3)(EtC{\equiv}CEt)_3}$ and tables of the data collection and refinement details, atom parameters, bond distances, bond angles, and least-squares planes for **2c**·$\mathrm{2CD_3CN}$ (13 pages); listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Chelate-Assisted, Pd-Catalyzed Efficient Carbonylation of Aryl Chlorides

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Palladium-catalyzed carbonylation of aryl halides under mild pressure forms the basis for a number of synthetically useful reactions, including the syntheses of carboxylic acids,[1,2] esters,[1,3] lactones,[1,4] amides[1,5] lactams,[1,6] keto esters, and keto amides,[7,8] and considerable effort has been devoted to the study of the scope and mechanisms of these reactions. One serious limitation common to all of these reactions, which hinders industrial utilization, is the fact that aryl chlorides, which are obviously more attractive as starting materials than the aryl bromides and iodides, are generally unreactive.[9] Recently, activation of aryl chlorides

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(9) Cobalt-catalyzed *photochemical* carbonylation of some aryl chlorides was reported,[9a] although in similar studies, no carbonylation was observed and *o*-dichlorobenzene could be used as a solvent.[9b] Co-catalyzed carbonylation of the activated chloronaphthalenes was reported, although chlorobenzene derivatives do not react:[9c] (a) Kudo, K.; Shibata, T.; Kashimura, T. *Chem. Lett.* **1987**, 577. (b) Brunet, J. J.; Sidot, C.; Caubere, P. *J. Org. Chem.* **1983**, *48*, 1166. (c) Foá, M.; Francalanci, F.; Bencini, E.; Gradano, A. *J. Organomet. Chem.* **1985**, *285*, 293.

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Table I. Pd-Catalyzed Carbonylation of Aryl Chlorides[a]

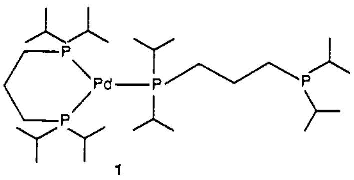
Ar	nucleophile	solvent	base	product	yield,[b] %
Ph	n-BuOH	n-BuOH	NaOAc	$PhCO_2Bu$	89 (100)[c]
Ph	MeOH	DMF	NaOAc	$PhCO_2Me$	78
Ph	MeOH	dioxane	NEt_3	$PhCO_2Me$	71
Ph	H_2O	DMF	NaOAc	$PhCO_2H$	70
Ph	n-Pr_2NH	DMF		$PhCONPr_2$	87
Ph	Et_2NH	xylene		$PhCONEt_2$	72
4-ClC_6H_4	MeOH	DMF	NaOAc	1,4-$C_6H_4(CO_2Me)_2$	82
4-MeC_6H_4	H_2O	DMF	NaOAc	4-$MeC_6H_4CO_2H$	79
4-$MeOC_6H_4$	n-BuOH	n-BuOH	NaOAc	4-$MeOC_6H_4CO_2Bu$	75
3-$MeOC_6H_4$	n-Pr_2NH	DMF		3-$MeOC_6H_4CONPr_2$	80
4-$MeOCOC_6H_4$	MeOH	DMF	NaOAc	1,4-$C_6H_4(CO_2Me)_2$	85

[a] Reaction conditions: A solution containing chlorobenzene (10 mmol), **1** (0.1 mmol), alcohol or water (1 mL), base (10 mmol), and solvent (3 mL) was heated at 150 °C for 20 h under 70 psi of CO. In amidation, 2 mL of amine was used. Similar results are obtained when $Pd(OAc)_2$ + 2dippp is used instead of **1**. [b] Isolated yield. [c] GC yield.

toward Pd-catalyzed carbonylation by stoichiometric utilization of their chromium tricarbonyl complexes was reported as a reaction of industrial significance.[10] Clearly, a method for direct catalytic carbonylation of aryl chlorides under mild pressure in one or more of these reactions would be of great interest. We report here that this is possible with the new complex $(dippp)_2Pd$ (or its precursors) as catalysts [dippp = bis(diisopropylphosphino)propane], leading to high-yield syntheses of carboxylic acids, esters, and amides from aryl chlorides.

Oxidative addition of an aryl halide to Pd(0) is thought to be a common step in all Pd-catalyzed aryl halide carbonylations. Assuming that the much-lower propensity of aryl chlorides, as compared with aryl bromides and iodides, to undergo this reaction[11] is the main reason for their lack of reactivity in carbonylation, we planned to increase the rate of this step without adversely affecting other steps in the catalytic cycle. Our approach was to utilize chelate-stabilized, electron-rich Pd(0) complexes.

The new complex $(dippp)_2Pd(0)$ (**1**) was prepared by nucleophilic cleavage of 2-methallylpalladium chloride dimer[12] with sodium methoxide in the presence of 2 equiv of dippp and was crystallized from a pentane solution at −30 °C. ^{31}P NMR reveals that it is present in solution in an "arm off", trigonal form.[13]



1

1 is an efficient catalyst for carbonylation of aryl chlorides (eq 1). For convenience, $Pd(OAc)_2$ + 2dippp can be used, generating the Pd(0) catalyst in situ under the reducing carbonylation conditions. Table I lists representative reactions of aryl chlorides, leading to high-yield syntheses of carboxylic esters, acids, and amides.

$$ArCl + NuH + CO + base \rightarrow ArCONu + base{\cdot}HCl \qquad (1)$$

$$Nu = OH, OCH_3, RNH$$

No catalyst deactivation or decomposition is observed. For example, upon addition of a new charge of chlorobenzene and sodium acetate to the reaction in 1-butanol, catalytic activity to yield more n-butyl benzoate is resumed.[14] As expected, the reactions are highly ligand dependent, pointing to the uniqueness of dippp (Table II).

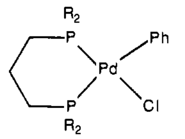
Table II. Ligand Dependence of Chlorobenzene Carbomethoxylation

ligand	conversion after 20 h,[a] %
$R_2P(CH_2)_nPR_2$	
n = 3, R = i-Pr (dippp)	80
n = 4, R = i-Pr (dippb)	40
n = 2, R = i-Pr (dippe)	30
n = 3, R = Ph (dppp)	15
n = 2, R = Me (dmpe)	3
n = 2, R = Ph (dppe)	2
PMe_3	0
$P(i\text{-}Pr)_3$	0
PPh_3	0

[a] A solution containing chlorobenzene (10 mmol), palladium acetate (0.1 mmol), sodium acetate (10 mmol), methanol (1 mL), DMF (3 mL), and diphosphine (0.2 mmol) or monophosphine (0.4 mmol) were heated at 150 °C under 70 psi of CO. Conversion is based on GC analysis.

Although the exact ligand requirements are unknown at this stage, chlorobenzene carbomethoxylation may require (1) chelation, (2) basicity (compare dippp > dppp; dippe > dppe), and (3) steric bulk, e.g., dippe > dmpe; (4) a six-membered chelate ring is optimal, the reactivity trend being dippp > dippb > dippe; dppp > dppe.

It seems that dippp is the optimal choice. Preliminary experiments of mechanistic relevance are the following: (1) reaction of **1** with CO is reversible, regenerating the starting complex under vacuum; (2) chlorobenzene undergoes oxidative addition to **1** at 50 °C (in hexane), yielding complex **2**;[15] the reaction is slow and requires several days for completion; (3) carbonylation of **2** at 50 psi yields complex **3**[16] quantitatively; (4) addition of Et_3N to a methanolic solution of **3** at 25 °C results in *instantaneous* decomposition to yield methyl benzoate.



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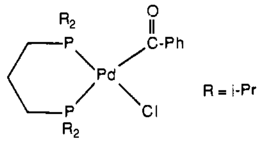

3

These observations suggest that oxidative addition of chlorobenzene is the slowest step in carbalkoxylation catalysis by **1**. For comparison, iodobenzene carbalkoxylation catalyzed by PR_3 complexes involves rate-determining alcoholysis of an acylpalladium complex.[7,17] A kinetic study[7] indicates that this step involves predissociation of a phosphine ligand. The unusual facility of the nucleophilic cleavage of **3**[18] may be the result of the relative

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(13) $^{31}P[^1H]$ NMR of **1** (toluene-d_8): δ 1.0 (s, 1 P), 45.3 (t, J = 84 Hz, 1 P), 21.4 (d, J = 84 Hz, 2 P).

(14) At the sacrifice of the rate, it is possible to use substrate:catalyst ratios of below 100:1, although the lowest practical catalyst concentration has not been determined.

(15) $^{31}P[^1H]$ NMR of **2** (toluene-d_8): δ 28.7 (d, J = 42 Hz, 1 P), 11.0 (d, J = 42 Hz, 1 P).

(16) **3**: $^{31}P[^1H]$ NMR (toluene-d_8): δ 27.6 (d, J = 65 Hz, 1 P), 8.1 (d, J = 65 Hz, 1 P). IR: (Nujol) 1648 cm^{-1} (C=O).

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ease of opening the chelate ring because of (a) size, (b) bulkiness, and (c) a strong acyl-trans effect. Chelate opening may be important also in the CO insertion step.[19]

Chlorobenzene oxidative addition to **1** is also more facile compared to phenylphosphine palladium complexes. High electron density at the metal is undoubtedly one reason, but the low affinity of **1** for CO, leaving in solution a higher concentration of an unsaturated complex, may also be important. Clearly a number of factors may be involved in making **1** an efficient, unique catalyst.[20] This, as well as potential use of **1** and related complexes in other catalytic reactions, is under active investigation.

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(18) Alcoholysis of acylpalladium complexes containing monodentate phosphines requires heating[7,17] and appears to be much slower than that of **3**.

(19) The ligand dppp was recently observed to have an accelerating effect on the carbomethoxylation of the reactive aryl trifluoromethanesulfonates: Dolle, R. E.; Schmidt, S. J.; Kruse, L. I. *J. Chem. Soc., Chem. Commun.* **1987**, 904.

(20) The second dippp ligand may also play a role in the catalysis. Significantly lower yields are obtained when either **2** or **3** is utilized as catalyst.

Direct Observation of β-Hydride Elimination Reactions on Metal Surfaces

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In this communication we report direct evidence for a β-hydride elimination mechanism in hydrocarbon decomposition over metal surfaces. This pathway is perhaps the most common of the decomposition reactions in transition-metal alkyls containing β-hydrogens; there are many examples for such a mechanism in the organometallic literature.[1] β-Elimination has also been indirectly invoked when explaining mechanisms for hydrocarbon conversion over transition-metal catalysts.[2,3] However, due to the difficulty in forming alkyl moieties on metal surfaces, the direct detection of such processes has so far eluded surface scientists. We here present thermal programmed desorption (TPD) spectra from partly deuterated fragments chemisorbed on Pt(111) which unequivocally show that ethyl moieties decompose on those surfaces by β-hydrogen elimination to form adsorbed ethylene.

The experiments were performed in an ultrahigh-vacuum chamber equipped with surface-sensitive instrumentation, as described in detail elsewhere.[4] Ethyl groups were formed on the platinum surface by saturation with ethyl iodide at liquid nitrogen temperatures followed by annealing above 170 K. Using X-ray photoelectron (XPS) and reflection-absorption infrared (RAIRS) spectroscopies, we have previously shown that this procedure conduces to the breaking of the C-I bond with the concurrent formation of ethyl moieties,[5,6] and Lloyd et al. have recently used high-resolution electron energy loss spectroscopy (HREELS) to

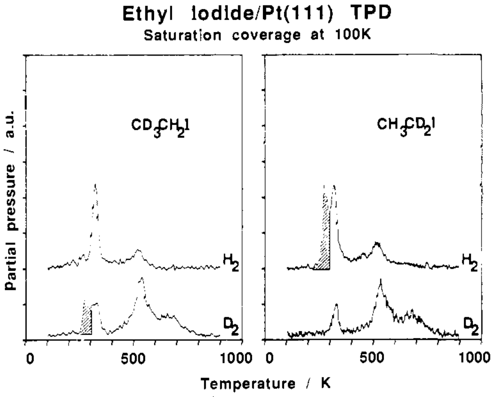

Figure 1. H_2 and D_2 thermal programmed desorption (TPD) spectra from saturation coverages of CD_3CH_2I (left) and CH_3CD_2I (right) on Pt(111). The peaks corresponding to the first decomposition step (a β-hydride elimination) are highlighted.

demonstrate that ethyl groups are stable on Pt(111) below 230 K.[7]

Adsorbed ethyl decomposes thermally above 230 K to yield a new intermediate with C_2H_4 stoichiometry. This conversion has been studied by XPS,[5] HREELS,[7] and TPD.[5,7] Hydrogen (H_2) thermal desorption from CH_3CH_2I displays several peaks, the first at 275 K which corresponds to one-fifth of the total area under the spectrum (one out of five hydrogen atoms in CH_3CH_2I).[5] Here we have used partly deuterated ethyl iodide compounds in order to determine the origin of that first desorption feature. Figure 1 shows TPD spectra for H_2 and D_2 desorption from both adsorbed CD_3CH_2I and CH_3CD_2I. It is clear from the data that in the case of CD_3CH_2I the first desorption peak is composed almost exclusively of deuterium gas, while for CH_3CD_2I this feature is only seen in the H_2 trace (shadowed areas in the figure). These results clearly indicate that the hydrogen atom extracted in the first decomposition step of ethyl chemisorbed on Pt(111) comes from the β position. Additional TPD, XPS, and HREELS data has been used to determine that chemisorbed ethylene forms as a result of ethyl decomposition, corroborating the proposed β-hydride elimination mechanism.[5,7] Adsorbed ethylene then reacts to form ethylidyne by going through a vinyl intermediate.[5,8] This reaction starts at temperatures as low as 260 K, but its rate peaks around 305 K in TPD experiments.[9]

This is, to the best of our knowledge, the first study showing that a β-hydride elimination mechanism is operative in the decomposition of chemisorbed alkyls, in an analogous fashion to well-known chemistry for organometallic compounds. A particularly interesting example has been given recently by Brown et al., in which an ethyldiplatinum(I) complex was synthesized by starting from ethyl iodide and $Pt_2(\mu\text{-}Ph_2PCH_2PPh_2)_3$.[10] This compound undergoes β-H elimination at temperatures between 60 and 100 °C to yield ethylene and ethane. Ethane formation was also seen in our system.[5] Establishing the viability of the β-H elimination pathway on surfaces has clear implications in determining the mechanism for catalytic H-D exchange and hydrogenolysis of alkanes.[2,3] In particular, ethane H-D exchange on Pt(111) yields d_1- and d_6-substituted molecules predominantly. This product distribution can be explained by a mechanism involving ethyl groups as a common intermediate, which then reacts further by following two competitive pathways.[11,12] An additional intermediate with C_2H_4 stoichiometry is required to explain the high yield of fully deuterated ethane.[12] Previous data suggested

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