# Bimetallic Activation in Homogeneous Catalysis. 3. Mechanistic Study of the Methoxycarbonylation of Tricarbonyl(chlorobenzene)chromium: Isolation and Reactivity of Possible Reaction Intermediates

Véronique Dufaud,[†] Jean Thivolle-Cazat,[†] Jean-Marie Basset,*[,†] René Mathieu,[‡] Joël Jaud,[§] and Jacqueline Waissermann[∥]

*Institut de Recherches sur la Catalyse, Conventionné avec l'Université Claude Bernard, CNRS, 2 Av. Albert Einstein, 69626 Villeurbanne Cédex, France, Laboratoire de Chimie de Coordination, 205 Route de Narbonne, 31077 Toulouse Cédex, France, CEMES-LOE/CNRS, 29 Rue Jeanne Marvig, BP 4347, 31055 Toulouse Cédex, France, and Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, 4 Pl. Jussieu, 75252 Paris Cédex 05, France*

*Received April 16, 1991*

The coordination of the $Cr(CO)_3$ moiety to the aromatic ring allows the carbonylation of chlorobenzene, catalyzed by palladium complexes, to esters, aldehydes, amides or α-oxo-amides. The mechanism of methoxycarbonylation of tricarbonyl(chlorobenzene)chromium, $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$, and the role of the $Cr(CO)_3$ moiety are now investigated. Tricarbonyl(chlorobenzene)chromium reacts at room temperature with $Pd(PPh_3)_4$ or $Pd(dba)_2$ and $PR_3$ via an oxidative addition to give aryl–palladium complexes of the type $\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Cl)L_y\}_{2/y}$, which are monomers (L = $PPh_3$ (**1**), $PEt_2Ph$ (**4**), $PPh_2Et$ (**5**)) or dimers (L = $PPh_3$ (**2**), $PCy_3$ (**3**)). By comparison, the oxidative addition of PhCl to $Pd(PPh_3)_4$ is known to proceed at 140 °C, indicating that the coordination of $Cr(CO)_3$ to PhCl greatly enhances the rate of this reaction. However, this reaction does not proceed with $L_2$ = dppe or dpph, but the same complexes can be prepared by Cl-bridge cleavage and/or phosphine exchange with $PR_3$ on $Pd_2[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PPh_3)_2$ to give the monomers (L = $PEt_2Ph$ (**4**), $PPh_2Et$ (**5**); $L_2$ = dppe (**6**), dpph (**7**)) and the dimer (L = $PCy_3$ (**3**)). The X-ray structures of complexes *trans*-$Pd_2[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PCy_3)_2$ (**3**) and *cis*-$Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3]Cl$ (dppe) (**6**) have been determined. Crystal data for **3**: orthorhombic with the space group *Pccm*; $a$ = 18.486 (8) Å, $b$ = 20.401 (7) Å, $c$ = 17.255 (6) Å, $V$ = 6508 Å$^3$, $Z$ = 8. Crystal data for **6**: monoclinic with the space group $P2_1/n$, $a$ = 9.841 (2) Å, $b$ = 12.783 (5) Å, $c$ = 28.377 (2) Å, $\beta$ = 92.23 (1)°, $V$ = 3567 Å$^3$, $Z$ = 4. These aryl–palladium complexes react at room temperature with CO under atmospheric pressure (L = $PPh_3$, $PEt_2Ph$; $L_2$ = dpph) or 5 bar (L = $PCy_3$) to give the corresponding monomeric or dimeric acyl–palladium complexes of the type $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3](Cl)L_y\}_{2/y}$ ($y$ = 2: L = $PPh_3$ (**8**), $PEt_2Ph$ (**9**), $L_2$ = dpph (**10**); $y$ = 1: L = $PPh_3$ (**11**), $PCy_3$ (**12**)). The reaction does not proceed with $L_2$ = dppe even under 30 bar of CO; Cl-bridge cleavage and phosphine exchange with dppe on $Pd_2[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PPh_3)_2$ enable the formation of *cis*-$Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]Cl$(dppe) (**13**). Methanolysis of complexes $Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]Cl(PPh_3)_2$ (**8**) and $Pd_2[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PPh_3)_2$ (**11**) in the presence of triethylamine at room temperature proceeds rapidly and leads to the formation of $(\eta^6\text{-}C_6H_5COOMe)Cr(CO)_3$, which is the product of methoxycarbonylation of $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$. Complexes $\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3]Cl(PPh_3)_y\}_{2/y}$ (**1**, **2**) and $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]Cl(PPh_3)_y\}_{2/y}$ (**8**, **11**) then appear to be reasonable intermediates in the catalytic cycle of methoxycarbonylation of $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$. A possible mechanism for this reaction is discussed.

## Introduction

The alkoxycarbonylation of halogenated aromatics, catalyzed by complexes of palladium, is a reaction that has been studied for several years (eq 1).[1-5]

$$ArX + CO + ROH + base \xrightarrow{Pd\ cat.} ArCOOR + base\text{–}HX \quad (1)$$

However, until recently it was limited to bromides and iodides; aryl chlorides, which are less expensive raw materials, were usually found to be unreactive. The difficulty with carbonylating chloroaromatic compounds is probably due to the high temperature required to perform the first step of oxidative addition of the C–Cl bond to the zerovalent palladium active species. Since this elementary reaction can be compared to a nucleophilic substitution,[6] two different approaches were recently developed: (a) use of specific zerovalent palladium complexes rendered more nucleophilic and coordinatively unsaturated by basic and bulky phosphines like tricyclohexylphosphine[7] or bis(diisopropylphosphino)propane,[8] (b) coordination of the $Cr(CO)_3$ moiety to the aromatic ring of various aryl chlorides.

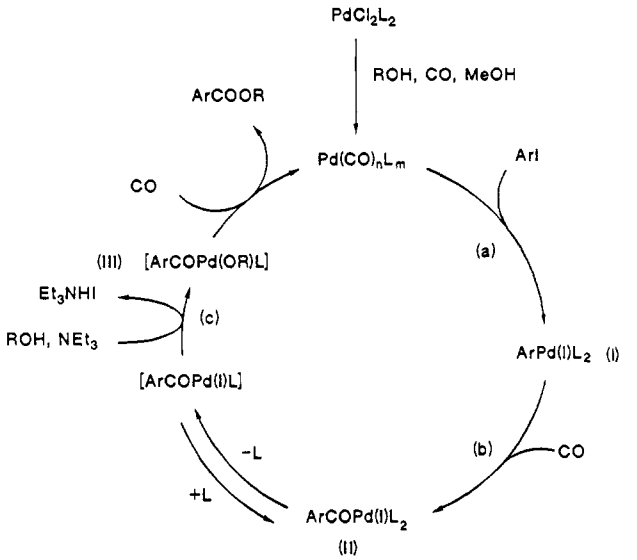
The latter allowed the carbonylation of tricarbonyl(chloroarene)chromium to the corresponding free or chromium-coordinated esters, aldehydes, amides,[9] or α-oxo-amides.[10] In this case, the $Cr(CO)_3$ entity, which is

[†] Institut de Recherches sur la Catalyse.
[‡] Laboratoire de Chimie de Coordination.
[§] CEMES-LOE.
[∥] Université Pierre et Marie Curie.

(1) Heck, R. F. *Adv. Catal.* **1977**, *26*, 323.
(2) Shoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318.
(3) Stille, J. K.; Wong, P. K. *J. Org. Chem.* **1975**, *40*, 532.
(4) Hidai, M.; Hikita, T.; Wada, Y.; Fujikura, Y.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2075.
(5) Ito, T.; Mori, K.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2091.
(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 306.
(7) Huser, M.; Youinou, M. T.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1386.
(8) Ben David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989**, *111*, 8742.
(9) Mutin, R.; Lucas, C.; Thivolle-Cazat, J.; Dufaud, V.; Dany, F.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 896.

0276-7333/91/2310-4005$02.50/0 

**Scheme I. Mechanism of Alkoxycarbonylation of Phenyl Iodide Proposed by Yamamoto and Used as a Basis in This Study**




known for its electron-withdrawing properties,[11] likely favors the oxidative addition step by lowering the electron density of the chloroaromatic ring.[12] Then, at least in the first step of the catalytic cycle, a bimetallic activation of the chloroaromatic compounds is expected, leading to an aryl intermediate $\sigma$-coordinated to palladium and $\pi$-coordinated to chromium.

The concept of bimetallic activation has led us to study the different steps of the mechanism of methoxycarbonylation of tricarbonyl(chlorobenzene)chromium. We have assumed that the catalytic cycle of this reaction is similar to that proposed by Yamamoto et al.[13] for the alkoxycarbonylation of iodobenzene (Scheme I) but with $Cr(CO)_3$ coordinated intermediates.

The main steps of Yamamoto's mechanism are the following (Scheme I): (a) oxidative addition of an aryl halide to a zerovalent palladium complex leading to a $\sigma$-aryl–Pd species (I), (b) insertion of a CO molecule into the C–Pd bond, giving rise to the formation of an acyl–Pd complex (II), (c) alcoholysis of the last compound, in the presence of a base leading, probably by a multistep process, to the formation of the ester.

Garrou and Heck were the first to propose the main features of this mechanism;[14] they showed that the last step of ester formation does not proceed via the alcoholysis of a reductively eliminated aroyl halide but directly via that of the acyl intermediate; however Yamamoto et al.[13] showed that this step probably involves an acyl(alkoxy)-palladium intermediate (III) rather than a direct nucleophilic attack of the alcohol on the acyl group. Although such a compound could not be isolated during treatment of the acyl–Pd complex by a methanol/triethylamine mixture, acyl(aryloxy)palladium compounds obtained by another route gave the corresponding ester by reductive elimination.[15]

The role of a halo(bisphosphine)(carbomethoxy)palladium intermediate was previously suggested by Stille and Wong[3] since such complexes can be formed by reaction of a catalyst precursor $PdCl_2L_2$ with CO, methanol, and triethylamine;[16] however, while this complex can react further with methyl iodide or benzyl bromide to yield ester,[16] no reaction was observed by Moser et al. in the case of bromobenzene.[17] Finally, Milstein[18] also demonstrated that an aryl(carbomethoxy)palladium complex eventually formed after the oxidative addition step could not lead to the ester.

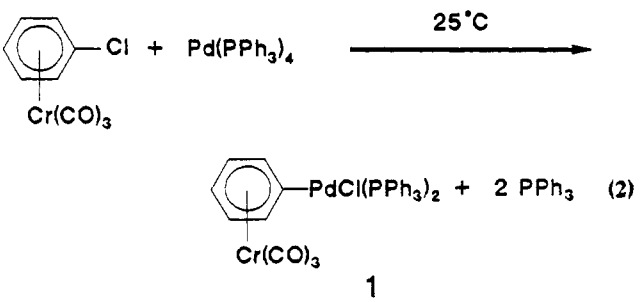
The strategy followed in this work was to carry out the synthesis of postulated bimetallic intermediates and to study their stepwise transformation into the final tricarbonyl(methylbenzoate)chromium. For this purpose a variety of phosphine or diphosphine ligands was used.

## Results

The different paths for preparation of the various intermediates are summarized in Scheme II. Their characterization is given in Table VI.

**A. Preparation of Aryl–Palladium Complexes of the Type $\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Cl)L_y\}_{2/y}$.** These complexes are assumed to be the first intermediates in the catalytic cycle of carbonylation (Scheme III). Depending on the preparation conditions, monomers or dimers can be formed. Two methods have been used to obtain such compounds: the first one is based on oxidative addition of tricarbonyl(chlorobenzene)chromium to zerovalent palladium complexes and the second one on phosphine ligand exchange on Pd(II) complexes.

**1. Oxidative Addition of Tricarbonyl(chlorobenzene)chromium to Zerovalent Palladium Complexes.** $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$ reacts easily at room temperature with 1 equiv of $Pd(PPh_3)_4$ to give a mixture of products in which $Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3]Cl(PPh_3)_2$ (1) is the major compound (eq 2).




(2)

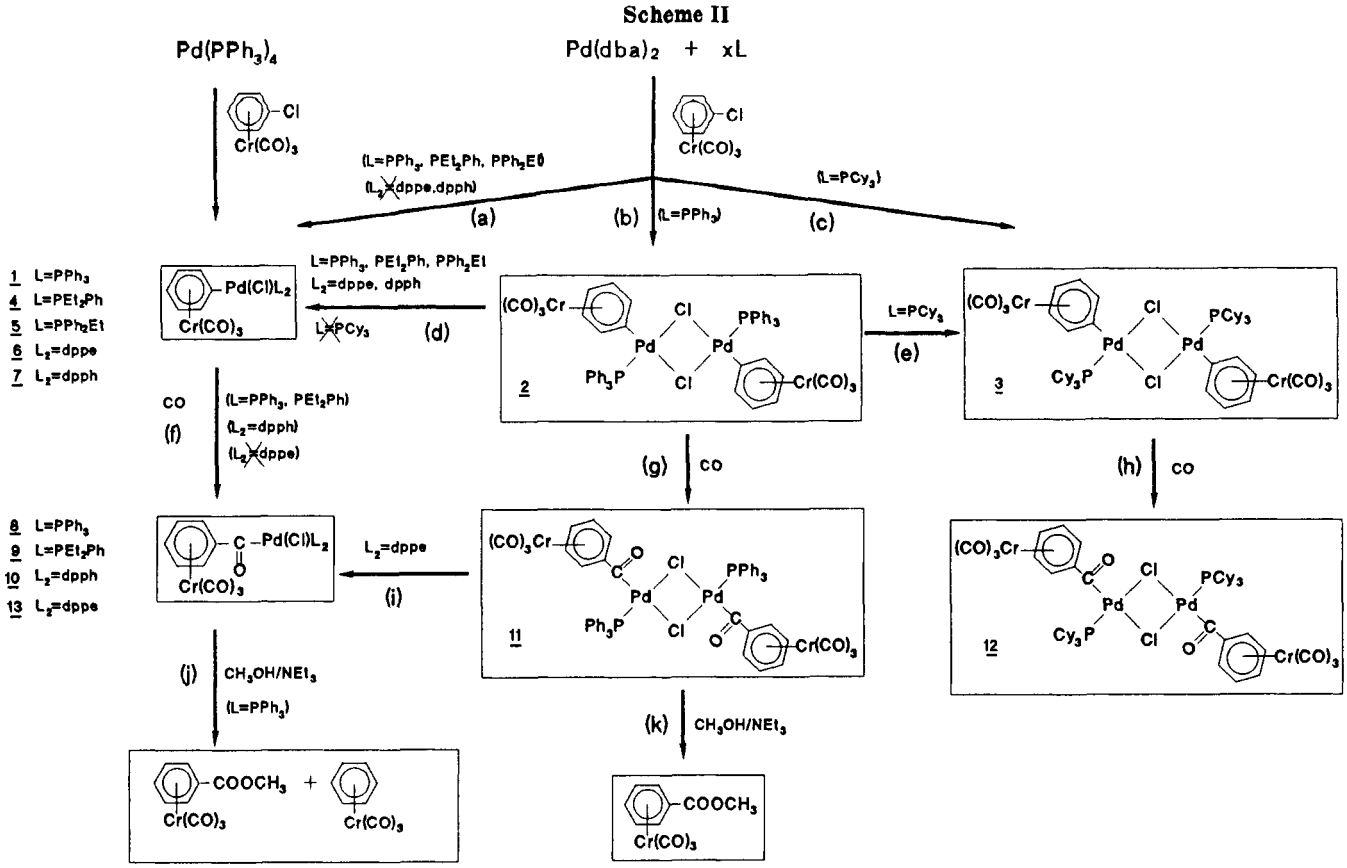
1

By comparison, chlorobenzene reacts with $Pd(PPh_3)_4$ to give $Pd(C_6H_5)Cl(PPh_3)_2$ at 140 °C,[19,20] which shows the dramatic enhancement of the rate of the oxidative addition of the C–Cl bond to zerovalent palladium by the $Cr(CO)_3$ moiety.

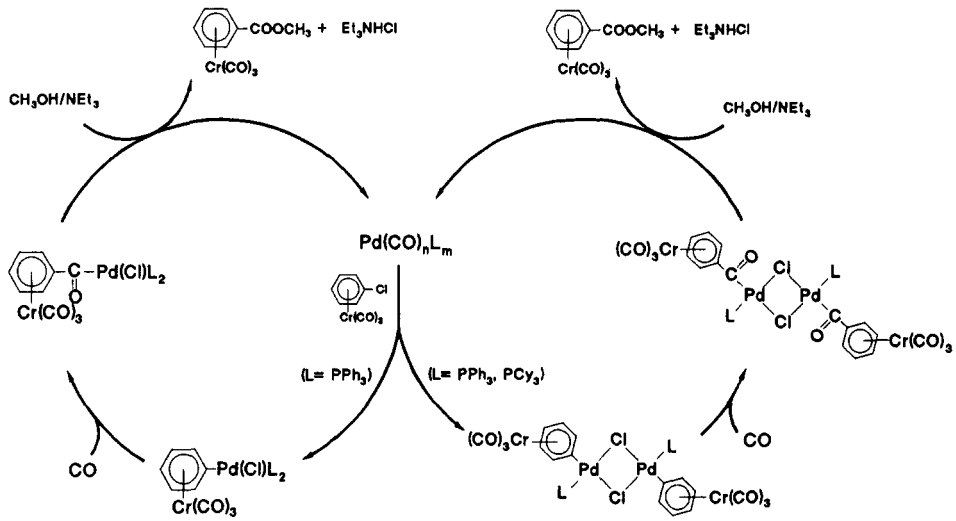
The infrared spectrum of 1 shows two bands at 1947 and 1867 $cm^{-1}$ attributable to the stretching vibrations of the

(10) Dany, F.; Mutin, R.; Lucas, C.; Dufaud, V.; Thivolle-Cazat, J.; Basset, J. M. *J. Mol. Catal.* **1989**, *51*, L15.
(11) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 651.
(12) The coordination of the $Cr(CO)_3$ moiety to chloroarenes has also been used for the palladium-catalyzed coupling to copper acetylides: Villemin, D.; Shigeko, E. *J. Organomet. Chem.* **1985**, *293*, C10. Tetraalkyltin or olefins: Scott, W. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1755. 1,4-Bis[(trimethylstannyl)ethynyl]benzene: Wright, M. E. *Macromolecules* **1989**, *22*, 3256.
(13) Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1987**, *6*, 1640.
(14) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.
(15) Komiya, S.; Akai, Y.; Tanaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.
(16) Hidai, M.; Kokura, M.; Uchida, Y. *J. Organomet. Chem.* **1973**, *52*, 431.
(17) Moser, W. R.; Wang, A. W.; Kildahl, N. K. *J. Am. Chem. Soc.* **1988**, *110*, 2816.
(18) Milstein, D. *J. Chem. Soc., Chem. Commun.* **1986**, 817.
(19) Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718.
(20) Coulson, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 1530.

**Scheme II**




**Scheme III**




carbonyls of the $Cr(CO)_3$ fragment. They are shifted by about 10 $cm^{-1}$ to lower wavenumbers in comparison to those of tricarbonyl(chlorobenzene)chromium; this indicates a modest electron flow to the chromium via the Pd–C bond.[21]

The sharp singlet observed at 235 ppm in the $^{13}C\{^1H\}$ NMR spectrum corresponding to the carbonyls of $Cr(CO)_3$ indicates that they are equivalent; it suggests a rapid rotation, relative to the NMR time scale, of the $Cr(CO)_3$ group along the chromium–arene axis, which is not perturbed by the ligands on palladium. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 25.4 ppm, pointing out the equivalence of the two phosphorus atoms. This suggests a trans configuration of the complex, which is generally observed for complexes of the same type without chromium.[14]

The secondary products of the reaction were identified by their $^{31}P\{^1H\}$ NMR chemical shifts in $C_6D_6$ as: $Pd_2[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PPh_3)_2$ (2) (35.18 ppm, vide infra), $Pd(C_6H_5)Cl(PPh_3)_2$ (24.6 ppm),[22] and $PdCl_2(PPh_3)_2$ (24.4 ppm). The presence of $Pd(C_6H_5)Cl(PPh_3)_2$ indicates that some decoordination of the $Cr(CO)_3$ moiety has taken place in 1 after the oxidative addition step, since chlorobenzene alone does not react with $Pd(PPh_3)_4$ at room temperature. This decoordination is likely due to the free phosphines released during oxidative addition, as these compounds are known to favor this process with complexes

(21) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 114.

(22) $Pd(C_6H_5)Cl(PPh_3)_2$ has been prepared by the reaction of $Pd(PPh_3)_4$ in refluxing chlorobenzene according to refs 19 and 20.

of the type $(\eta^6\text{-arene})Cr(CO)_3$.[23]

In order to prevent such a decoordination process, the use of another zerovalent palladium complex was considered: oxidative addition of aryl halides on dibenzylidene(phosphine)palladium complexes $Pd(PR_3)_2$(dba) was recently reported.[7,24] Various $[(\eta^6\text{-aryl})Cr(CO)_3]$(phosphine)chloropalladium complexes were prepared according to this method:

$$Pd(dba)_2 + xPR_3 + (\eta^6\text{-}C_6H_5Cl)Cr(CO)_3 \rightarrow (y/2)\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3]Cl(PR_3)_y\}_{2/y} + 2dba + (x - y)PR_3 \quad (3)$$

$$y = 1, 2$$

The complex $Pd(PR_3)_2$(dba) is assumed to be formed in situ, and the released dba ligand is expected not to displace the $Cr(CO)_3$ group.

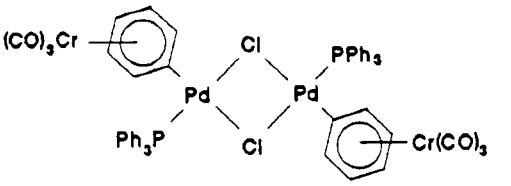
Thus, when tricarbonyl(chlorobenzene)chromium was allowed to react with 1 equiv of $Pd(dba)_2$[25] in the presence of 3 equiv of $PPh_3$ at room temperature, **1** was formed as the major compound with the same byproducts as previously obtained. When the same reaction was carried out with 1 equiv of $PPh_3$, the dimeric complex $Pd_2[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PPh_3)_2$ (**2**) could be obtained quantitatively.

The infrared spectrum of **2** displays the characteristic $\nu(CO)$ bands at 1947 and 1867 $cm^{-1}$ assigned to the carbonyls of the $Cr(CO)_3$ moiety. The $^1H$ NMR spectrum consists of two multiplets centered at 7.4 and 5 ppm with the relative intensities 3:1. The multiplet at 7.4 ppm is therefore assigned to the phenyl protons of the phosphines, and that at 5 ppm is assigned to the palladium-bound phenyl group; the slight upfield displacement of this latter may be due to shielding by electron density on palladium and to the coordination of the $Cr(CO)_3$ moiety.

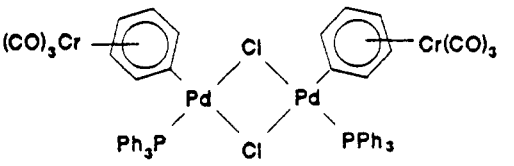
The three carbonyls of the $Cr(CO)_3$ fragment are equivalent ($^{13}C$ singlet at 235.56 ppm). The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at 35.17 ppm showing the equivalence of the two phosphorus atoms. As cis and trans configurations can be envisaged for **2**, it is unlikely that the two isomers show coincidental chemical shifts. A rapid isomerization process, by Cl-bridge cleavage, was proposed by Anderson to explain the occurrence of the singlet in $^{31}P\{^1H\}$ NMR spectra of similar complexes without chromium.[26] It is also reasonable to consider that only the trans configuration (A) exists, as in the case of $PCy_3$ (vide infra).

When reaction 3 is performed at room temperature with 2 equiv of tricyclohexylphosphine $PCy_3$, a pure dimeric complex $Pd_2[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2(\mu\text{-}Cl)_2(PCy_3)_2$ (**3**) is formed. Complex **3** has been characterized by IR, $^{31}P\{^1H\}$ NMR, and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 36.88 ppm showing the equivalence of the two phosphorus atoms. Single crystals of **3** could be obtained, allowing an X-ray structure determination (vide infra).

When reaction 3 is performed with 2 equiv of $PEt_2Ph$ or $PPh_2Et$, a mixture of products is obtained in which the expected monomeric complexes are effectively detected by $^{31}P$ NMR (vide infra). However an efficient separation of these products could not be achieved.



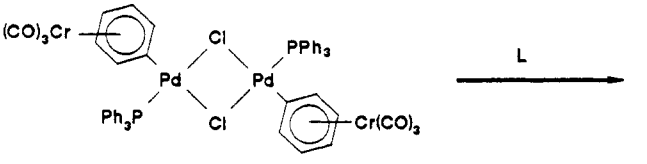

A



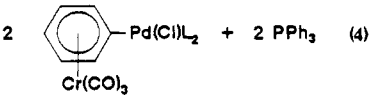

B

In contrast, reaction 3 does not proceed in the presence of 1 equiv of bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)hexane (dpph). In the case of dppe, the tricarbonyl(chlorobenzene)chromium was recovered and the complex Pd(dba)(dppe) was obtained quantitatively. This compound presents at $^{31}P\{^1H\}$ NMR spectrum with two doublets centered at 34.3 and 36.8 ppm ($^2J_{P-P}$ = 16 Hz); these data are consistent with those recently reported by Huser[24] and are specific for nonequivalent phosphorus atoms in the cis configuration on the metal. This nonequivalence can arise from a dissymetric coordination of the dba ligand. This well-defined NMR spectrum is indicative of an olefin ligand rigidly bonded to palladium; whereas, in the case of $Pd(dba)(PCy_3)_2$ the unresolved $^{31}P\{^1H\}$ NMR signal shows some fluxionality.[24] This difference in behavior of olefin complexes containing chelating ligands has already been observed in the case of platinum[27] or nickel[28] compounds, for which the rotation barrier of olefin proves to be higher. The absence of reactivity observed in the case of dppe and dpph ligands for reaction 3 may arise from a strongly bonded dba ligand to the palladium which, therefore, prevents attack on the C–Cl bond.

**2. Cleavage of Cl Bridges and Exchange of Phosphine in Complex 2.** A series of monomeric complexes of the type $Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Cl)L_2$ have been prepared quantitatively by treatment of the dimeric complex **2** with 2 equiv of diphosphine ($L_2$ = dppe, dpph) or 4 equiv of monophosphine (L = $PPh_2Et$, $PEt_2Ph$) (eq 4).




2




4 L= $PEt_2Ph$

5 L= $PPh_2Et$

6 $L_2$= dppe

7 $L_2$= dpph

(23) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 3, p 1037.

(24) Huser, M. Thesis, University Louis Pasteur of Strasbourg, 1988.

(25) Takahashi, Y.; Ito, T.; Sokai, S. Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

(26) Anderson, G. K. *Organometallics* **1983**, *2*, 665.

(27) Clark, H. C.; Ferguson, G.; Hampden-Smith, M. J.; Kaitner, B.; Ruegger, H. *Polyhedron* **1988**, *7*, 1349.

(28) Brauer, D. J.; Kruger, C. *J. Organomet. Chem.* **1974**, *77*, 423.

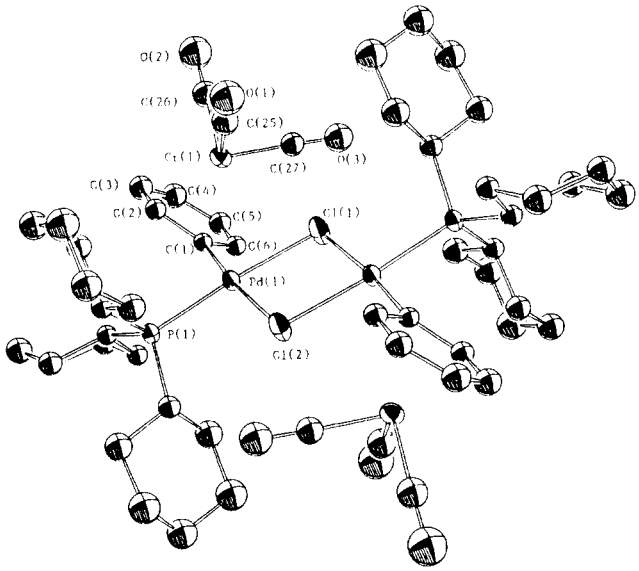



**Figure 1.** ORTEP plot of $\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Cl)PCy_3\}_2$ (**3**) with 50% probability ellipsoids.

**Table I. Crystallographic Data and Refinement Results for Complexes 3 and 6**

| | 3 | 6 |
|---|---|---|
| formula | $[PdClCrPO_3C_{27}H_{38}]_2 \cdot C_6D_6$ | $PdClCrP_2O_3C_{35}H_{29} \cdot CH_2Cl_2$ |
| mol wt | 1269.8 | 752.9 |
| temp, K | 293 | 293 |
| cryst syst | orthorhombic | monoclinic |
| space group | *Pccm* | $P2_1/n$ |
| *a*, Å | 18.486 (8) | 9.841 (2) |
| *b*, Å | 20.401 (7) | 12.783 (5) |
| *c*, Å | 17.255 (6) | 28.377 (2) |
| $\alpha$, deg | 90 | 90 |
| $\beta$, deg | 90 | 92.23 (1) |
| $\gamma$, deg | 90 | 90 |
| *Z* | 8 | 4 |
| vol, Å$^3$ | 6508 | 3567 (2) |
| cryst size, mm | block included in capillary of 0.15-mm radius | 0.1 × 0.3 × 0.4 |
| radiation | Mo K$\alpha$ | Mo K$\alpha$ |
| scan mode | $\omega/2\theta$ | $\omega/2\theta$ |
| scan range $\theta$, deg | 0.90 + 0.347 tan $\theta$ | 0.8 + 0.34 tan $\theta$ |
| no. of reflcn coll | 3494 | 6265 |
| no. of reflcn used (criteria) | 2723 [$I > 2\sigma(I)$] | 4031 [$I > 3\sigma(I)$] |
| computing program | CRYSTALS | CRYSTALS[42] |
| no. of variables | 269 | 499 |
| *R* | 0.0146 | 0.0373 |
| $R_w$[a] | 0.0442 | 0.0405 |
| $\sum$ shift/esd | 0.8 | 0.32 |
| residual electron density, e Å$^{-3}$ | 0.2 | 0.6 |

[a] $R_w = [\sum_i w_i(F_o - F_c)^2/\sum_i w_i F_o^2]^{1/2}$.

The reaction proceeds easily at room temperature with high yields (80–100%). This method shows that complexes **6** and **7**, which could not be obtained by oxidative addition reaction (eq 3), are in fact stable.

The $^{31}P\{^1H\}$ NMR spectra of **4**, **5**, and **7** show only one singlet, suggesting a trans configuration; the observation of an AB system with a coupling constant of 23 Hz in the $^{31}P\{^1H\}$ NMR spectrum of **6** indicates a nonequivalence of the two phosphorus atoms, and therefore a cis configuration is expected.

When **2** is allowed to react with 4 equiv of $PCy_3$, only the dimeric complex **3** is obtained (Scheme II, path e). No monomer was ever formed with $PCy_3$ either by oxidative addition or by phosphine exchange; this phosphine is likely able to break the Cl bridges in complex **2**, but its steric hindrance probably prevents the stabilization of a monomeric species, as can be visualized in the ORTEP diagram of **3** represented in Figure 1.

**Table II. Atomic Coordinates, Esd's, and Equivalent Isotropic Thermal Parameters for 3**

| atom | *x/a* | *y/b* | *z/c* | *U*(iso), Å$^2$ |
|---|---|---|---|---|
| Pd(1) | 0.44960 (3) | 0.46164 (3) | 0.07729 (4) | 0.0322 |
| Cr(1) | 0.24661 (8) | 0.44573 (6) | 0.01570 (8) | 0.0372 |
| P(1) | 0.4756 (1) | 0.4333 (1) | 0.2016 (1) | 0.0296 |
| Cl(1) | 0.4329 (1) | 0.4914 (1) | −0.0556 (1) | 0.0473 |
| O(1) | 0.0892 (4) | 0.4747 (5) | −0.0020 (5) | 0.0919 |
| O(2) | 0.2690 (4) | 0.4528 (4) | −0.1556 (4) | 0.0710 |
| O(3) | 0.2733 (5) | 0.5888 (4) | 0.0222 (5) | 0.0833 |
| C(1) | 0.3508 (4) | 0.4208 (4) | 0.0800 (5) | 0.0329 |
| C(2) | 0.3358 (4) | 0.3733 (4) | 0.0235 (5) | 0.0365 |
| C(3) | 0.2688 (5) | 0.3405 (4) | 0.0203 (6) | 0.0407 |
| C(4) | 0.2162 (5) | 0.3541 (5) | 0.0734 (7) | 0.0497 |
| C(5) | 0.2273 (5) | 0.4031 (5) | 0.1295 (5) | 0.0480 |
| C(6) | 0.2939 (5) | 0.4362 (4) | 0.1311 (5) | 0.0412 |
| C(7) | 0.4167 (4) | 0.3711 (4) | 0.2454 (5) | 0.0314 |
| C(8) | 0.4161 (5) | 0.3056 (4) | 0.2006 (5) | 0.0363 |
| C(9) | 0.3534 (5) | 0.2634 (4) | 0.2295 (6) | 0.0499 |
| C(10) | 0.3596 (5) | 0.2497 (5) | 0.3156 (6) | 0.0496 |
| C(11) | 0.3647 (6) | 0.3140 (5) | 0.3597 (6) | 0.0537 |
| C(12) | 0.4261 (6) | 0.3562 (4) | 0.3311 (5) | 0.0463 |
| C(13) | 0.4682 (4) | 0.5042 (4) | 0.2676 (5) | 0.0334 |
| C(14) | 0.3922 (5) | 0.5307 (4) | 0.2720 (5) | 0.0450 |
| C(15) | 0.3878 (6) | 0.5881 (5) | 0.3298 (6) | 0.0573 |
| C(16) | 0.4378 (7) | 0.6425 (5) | 0.3067 (6) | 0.0616 |
| C(17) | 0.5140 (7) | 0.6179 (5) | 0.3005 (7) | 0.0564 |
| C(18) | 0.5191 (5) | 0.5610 (5) | 0.2429 (6) | 0.0501 |
| C(19) | 0.5713 (5) | 0.4086 (4) | 0.2082 (5) | 0.0414 |
| C(20) | 0.6023 (6) | 0.4023 (5) | 0.2899 (6) | 0.0585 |
| C(21) | 0.6843 (6) | 0.3911 (7) | 0.2845 (7) | 0.0717 |
| C(22) | 0.7026 (5) | 0.3320 (6) | 0.2372 (8) | 0.0676 |
| C(23) | 0.6722 (6) | 0.3372 (6) | 0.1564 (8) | 0.0694 |
| C(24) | 0.5900 (5) | 0.3496 (6) | 0.1582 (7) | 0.0611 |
| C(25) | 0.1508 (5) | 0.4635 (6) | 0.0048 (6) | 0.0601 |
| C(26) | 0.2596 (5) | 0.4502 (4) | −0.0902 (5) | 0.0469 |
| C(27) | 0.2630 (6) | 0.5337 (5) | 0.0194 (6) | 0.0538 |
| C(31) | 0.4977 (6) | 0.7364 (7) | 0.0160 (9) | 0.117 (5) |
| C(32) | 0.4729 (7) | 0.7994 (6) | 0.0055 (9) | 0.121 (5) |
| C(33) | 0.4028 (8) | 0.8145 (6) | 0.0217 (9) | 0.122 (6) |
| C(34) | 0.3576 (6) | 0.7681 (7) | 0.052 (1) | 0.134 (6) |
| C(35) | 0.3837 (8) | 0.7059 (7) | 0.068 (1) | 0.154 (7) |
| C(36) | 0.4542 (8) | 0.6905 (6) | 0.0503 (9) | 0.133 (6) |

**Table III. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for 3**

| Distances | | | |
|---|---|---|---|
| Pd(1)–P(1) | 2.272 (2) | Cr(1)–C(2) | 2.218 (8) |
| Pd(1)–Cl(1) | 2.393 (2) | Cr(1)–C(3) | 2.187 (8) |
| Pd(1)–Cl(2) | 2.403 (2) | Cr(1)–C(4) | 2.191 (9) |
| Pd(1)–C(1) | 2.009 (7) | Cr(1)–C(5) | 2.178 (9) |
| Cr(1)–C(1) | 2.279 (8) | Cr(1)–C(6) | 2.182 (9) |
| **Angles** | | | |
| Cl(1)–Pd(1)–P(1) | 175.21 (8) | Cl(1)–Pd(1)–Cl(2) | 82.33 (8) |
| Cl(2)–Pd(1)–C(1) | 172.4 (3) | C(1)–Pd(1)–P(1) | 93.7 (2) |
| Cl(2)–Pd(1)–P(1) | 93.28 (8) | C(1)–Pd(1)–Cl(1) | 90.6 (2) |

Complex **2** reacts incompletely with 2 equiv of $PPh_3$ to form the monomeric complex **1** with the usual byproducts $Pd(C_6H_5)Cl(PPh_3)_2$ and $PdCl_2(PPh_3)_2$; the fact that the reaction is incomplete with $PPh_3$ suggests that this ligand is more weakly coordinated than the other phosphines.

**3. X-ray Crystallography of Complexes 3 and 6.** Table I gives a summary of crystal data and refinement results obtained for compound **3**. Positional parameters and equivalent isotropic thermal parameters are given in Table II. Figure 1 shows an ORTEP drawing of **3**, and Table III gives selected bond distances and bond angles for this compound.

Complex **3** has the expected dimeric structure with $\mu$-chloro bridges. The molecule has a symmetry center situated in the Pd, Cl, Pd, Cl rhomb. Therefore the two

**Table IV. Atomic Coordinates, Esd's, and Thermal Parameters for 6**

| atom | x/a | y/b | z/c | U(eq), Å² | U(iso), Å² |
|---|---|---|---|---|---|
| Pd(1) | 0.34545 (5) | 0.16648 (3) | 0.15344 (2) | 0.0374 | |
| Cr(2) | 0.36908 (9) | 0.30345 (7) | 0.02661 (3) | 0.0418 | |
| Cl(3) | 0.2170 (2) | 0.3220 (1) | 0.15637 (5) | 0.0506 | |
| P(4) | 0.4581 (2) | 0.0160 (1) | 0.15073 (5) | 0.0409 | |
| P(5) | 0.2963 (2) | 0.1146 (1) | 0.23000 (6) | 0.0438 | |
| C(6) | 0.4853 (7) | −0.0325 (5) | 0.2108 (2) | 0.0519 | |
| C(7) | 0.3548 (7) | −0.0206 (5) | 0.2368 (2) | 0.0568 | |
| C(8) | 0.4343 (6) | 0.2144 (5) | 0.0927 (2) | 0.0410 | |
| C(9) | 0.4618 (6) | 0.1565 (5) | 0.0514 (2) | 0.0436 | |
| C(10) | 0.5412 (6) | 0.1972 (5) | 0.0155 (2) | 0.0512 | |
| C(11) | 0.5927 (6) | 0.2999 (6) | 0.0189 (2) | 0.0565 | |
| C(12) | 0.5645 (6) | 0.3596 (5) | 0.0582 (2) | 0.0544 | |
| C(13) | 0.4867 (6) | 0.3178 (5) | 0.0944 (2) | 0.0485 | |
| C(14) | 0.3454 (7) | 0.3235 (6) | −0.0368 (2) | 0.0586 | |
| O(15) | 0.3321 (6) | 0.3358 (5) | −0.0768 (2) | 0.0894 | |
| C(16) | 0.2013 (6) | 0.2452 (5) | 0.0272 (2) | 0.0555 | |
| O(17) | 0.0932 (5) | 0.2077 (5) | 0.0273 (2) | 0.0859 | |
| C(18) | 0.2921 (7) | 0.4317 (5) | 0.0395 (3) | 0.0606 | |
| O(19) | 0.2485 (6) | 0.5109 (4) | 0.0480 (2) | 0.0832 | |
| C(20) | 0.6247 (6) | 0.0174 (5) | 0.1254 (2) | 0.0415 | |
| C(21) | 0.6577 (6) | −0.0437 (5) | 0.0873 (2) | 0.0503 | |
| C(22) | 0.7816 (7) | −0.0322 (6) | 0.0672 (3) | 0.0651 | |
| C(23) | 0.8716 (7) | 0.0396 (7) | 0.0848 (3) | 0.0697 | |
| C(24) | 0.8427 (8) | 0.0987 (7) | 0.1225 (3) | 0.0785 | |
| C(25) | 0.7189 (7) | 0.0874 (6) | 0.1436 (3) | 0.0658 | |
| C(26) | 0.3576 (6) | −0.0837 (5) | 0.1201 (2) | 0.0455 | |
| C(27) | 0.3876 (7) | −0.1895 (5) | 0.1253 (2) | 0.0590 | |
| C(28) | 0.3098 (8) | −0.2638 (6) | 0.1025 (3) | 0.0668 | |
| C(29) | 0.2006 (8) | −0.2348 (6) | 0.0741 (3) | 0.0670 | |
| C(30) | 0.1689 (7) | −0.1303 (6) | 0.0680 (3) | 0.0677 | |
| C(31) | 0.2482 (6) | −0.0550 (5) | 0.0916 (3) | 0.0562 | |
| C(32) | 0.4101 (6) | 0.1877 (5) | 0.2701 (2) | 0.0473 | |
| C(33) | 0.4527 (7) | 0.1493 (8) | 0.3141 (2) | 0.0737 | |
| C(34) | 0.5392 (8) | 0.207 (1) | 0.3438 (3) | 0.0854 | |
| C(35) | 0.5841 (8) | 0.3015 (9) | 0.3289 (3) | 0.0876 | |
| C(36) | 0.544 (1) | 0.3419 (7) | 0.2861 (4) | 0.0942 | |
| C(37) | 0.4584 (8) | 0.2827 (6) | 0.2561 (3) | 0.0739 | |
| C(38) | 0.1295 (6) | 0.1178 (5) | 0.2558 (2) | 0.0474 | |
| C(39) | 0.1022 (7) | 0.0579 (6) | 0.2950 (3) | 0.0624 | |
| C(40) | −0.0245 (8) | 0.0623 (6) | 0.3141 (3) | 0.0761 | |
| C(41) | −0.1239 (7) | 0.1240 (6) | 0.2949 (3) | 0.0680 | |
| C(42) | −0.0979 (7) | 0.1848 (6) | 0.2568 (3) | 0.0679 | |
| C(43) | 0.0291 (7) | 0.1824 (6) | 0.2365 (2) | 0.0590 | |
| C(1) | 0.901 (1) | 0.3665 (8) | 0.0980 (3) | 0.1133 | |
| Cl(1) | 0.828 (1) | 0.3872 (6) | 0.1550 (3) | | 0.1168 (9) |
| Cl(2) | 0.9136 (7) | 0.4896 (5) | 0.0697 (2) | | 0.1168 (9) |
| Cl(11) | 0.840 (1) | 0.4100 (6) | 0.1472 (3) | | 0.1168 (9) |
| Cl(12) | 0.9070 (7) | 0.4493 (5) | 0.0517 (2) | | 0.1168 (9) |

$(\eta^6\text{-}C_6H_5)Cr(CO)_3$ moieties $\sigma$-bonded to the two palladium atoms are in a trans configuration, as expected from $^{31}P$ NMR data. The complex adopts an almost square-planar geometry around each palladium atom. Interestingly, the dihedral angle between the $\sigma$-bonded aryl ligand and the coordination plane is 56°, instead of 90° for similar aryl–Pd complexes like $Pd(C_6H_5)Cl(PCy_3)_2$,[7] Pd[(phenylazo)-phenyl]$Cl(PEt_3)_2$,[29] or $Pd(Me(NO)NC_6H_4)Cl(PPh_3)_2$.[30] This suggests the occurrence of some steric constraints brought by the $Cr(CO)_3$ group. All distances are in agreement with values given for $(\eta^6$-arene$)Cr(CO)_3$ compounds[31] and similar palladium complexes mentioned above. For example with $Pd(C_6H_5)Cl(PCy_3)_2$,[7] bond lengths are Pd–P(1) 2.343 (1), Pd–P(2) 2.347 (1), Pd–Cl 2.403 (1), and Pd–C 2.004 (6) Å, whereas for **3**, they are Pd–P 2.272 (2), Pd–Cl(1) 2.393 (2), Pd–Cl(2) 2.403 (2), and Pd–C 2.009 (7) Å. Only the Pd–P bond appears somewhat shorter in **3**; the $Cr(CO)_3$ moiety does not bring modification in the Pd–C and the trans Pd–Cl bonds lengths. As

(29) Weaver, D. L. *Inorg. Chem.* **1970**, *9*, 2250.
(30) Constable, A. G.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 2282.
(31) Sneeden, R. P. A. In *Organochromium Compounds*; Maitlis, P. M., Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1975; p 115.

**Table V. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for 6**

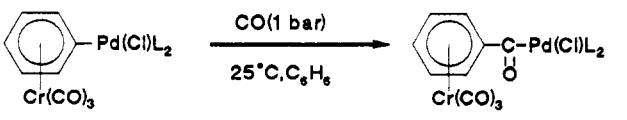
| | | | |
|---|---|---|---|
| **Distances** | | | |
| Pd(1)–Cl(3) | 2.359 (2) | Cr(2)–C(8) | 2.266 (6) |
| Pd(1)–P(4) | 2.223 (2) | Cr(2)–C(9) | 2.193 (6) |
| Pd(1)–P(5) | 2.340 (2) | Cr(2)–C(10) | 2.204 (6) |
| Pd(1)–C(8) | 2.056 (6) | Cr(2)–C(11) | 2.220 (6) |
| P(4)–C(6) | 1.825 (6) | Cr(2)–C(12) | 2.210 (6) |
| P(5)–C(7) | 1.830 (7) | Cr(2)–C(13) | 2.215 (6) |
| C(6)–C(7) | 1.513 (9) | | |
| **Angles** | | | |
| P(4)–Pd(1)–Cl(3) | 177.51 (6) | C(8)–Pd(1)–P(4) | 90.0 (2) |
| C(8)–Pd(1)–P(5) | 166.6 (2) | P(5)–Pd(1)–Cl(3) | 94.34 (6) |
| P(5)–Pd(1)–P(4) | 84.75 (6) | C(8)–Pd(1)–Cl(3) | 91.4 (2) |
| C(6)–P(4)–Pd(1) | 108.5 (2) | C(7)–P(5)–Pd(1) | 106.9 (2) |
| C(7)–C(6)–P(4) | 108.9 (4) | C(6)–C(7)–P(5) | 108.2 (5) |

in compound $Pd_2(C_2H_4)_2(\mu\text{-}Cl)_2Cl_2$,[32] the bridging chlorines bring some distortion in the square-planar geometry about palladium since the Cl(1)–Pd–Cl(2) angle is only 82.33 (8)°; but in **3**, the two Pd–Cl bonds lengths are equal, suggesting a similar trans effect from the $PCy_3$ ligand and the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ group.

Table I also gives a summary of crystal data and refinement results obtained for compound **6**. Table IV gives positional and thermal parameters. Figure 2 shows an ORTEP drawing of $Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3]Cl$(dppe) **6**, and Table V gives selected bond distances and bond angles.

The palladium atom is four-coordinated and surrounded by the chlorine atom, the $\sigma$-bonded carbon atom of the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ moiety, and the two phosphorus atoms of the dppe ligand in cis position, as expected from $^{31}P$ NMR spectroscopy. The complex adopts an almost square-planar geometry around the palladium atom. The slight deviation from ideal geometry is particularly reflected by the value of the angles P(4)–Pd–Cl of 177.51° and C–Pd–P(5) of 166.6°, which are lower than 180°. The low value for the angle P(4)–Pd–P(5) (84.75°) can be explained by the chelating structure of the diphosphine ligand. All distances are in agreement with values obtained in similar $(\eta^6$-arene$)Cr(CO)_3$ and palladium compounds. There is a slight difference between the two Pd–P bonds lengths (Pd–P(4) 2.223, and Pd–P(5) 2.340 Å), which may be due to the higher trans effect of the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ group compared to that of the chlorine. The $\sigma$-bonded aryl ligand is not perpendicular to the coordination plane and presents a dihedral angle of 47.43°.

**B. Preparation of Aroyl–Palladium Complexes of the Type $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3]Cl(PR_3)_y\}_{2/y}$. 1. Carbonylation of Aryl-Type Palladium Complexes (Scheme II, Path f, g, h).** When CO is bubbled through a benzene solution of **1**, **4**, or **7** for 2 h at room temperature, the related aroyl complexes are obtained:




1 L= $PPh_3$ 8 L= $PPh_3$
4 L= $PEt_2Ph$ 9 L= $PEt_2Ph$
7 $L_2$= dppb 10 $L_2$= dppb

(5)

In the case of **6** where $L_2$ = dppe, the formation of the corresponding acyl complex is not observed even under a

(32) Dempsey, J. N.; Baenziger, N. C. *J. Am. Chem. Soc.* **1955**, *77*, 4984.

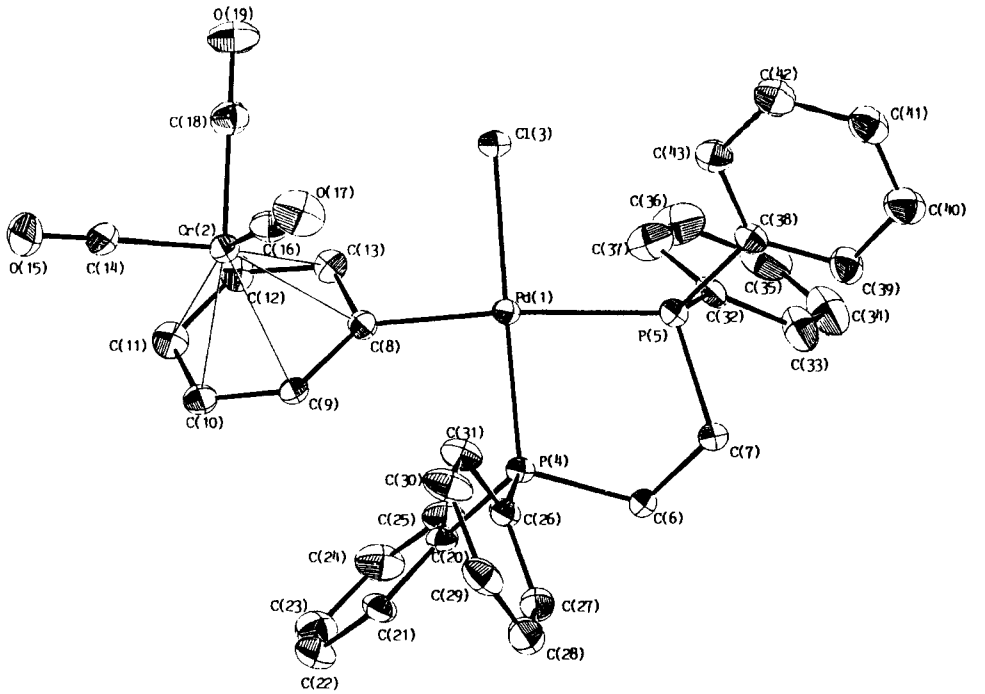
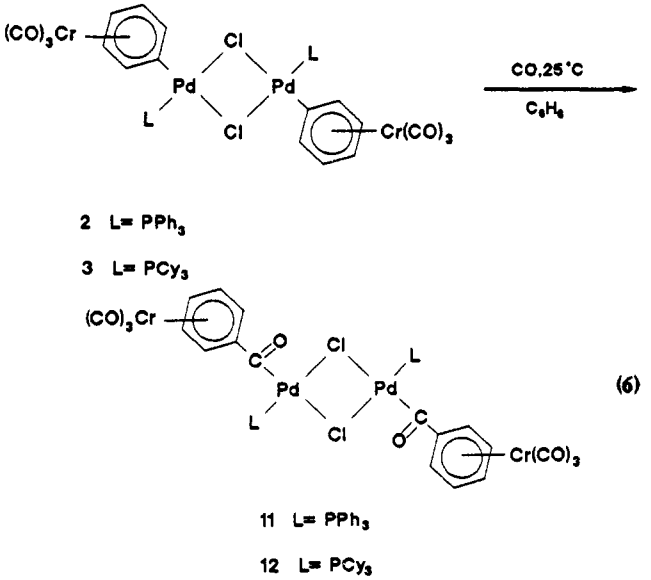



**Figure 2.** ORTEP plot of $Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3]Cl(dppe)$ (**6**) with 50% probability ellipsoids.

CO pressure of 30 bar. It is likely due to the strong chelating effect of the dppe ligand, which does not allow the liberation of a coordination site for CO.

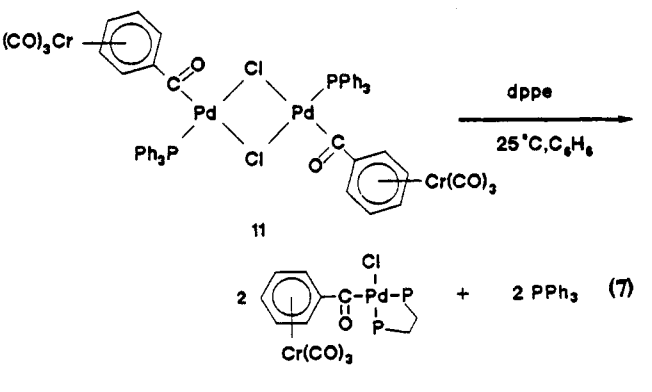
The dimeric complexes **2** and **3** can also be carbonylated in the same way at room temperature under 1 and 5 bar of CO, respectively. After several hours, the corresponding aroyl complexes are obtained (eq 6).




The infrared spectra of all the prepared complexes **8–12** display a characteristic CO stretching band in the range 1639–1657 $cm^{-1}$ assigned to an acyl group (Table VI); the CO stretching vibrations of the $Cr(CO)_3$ group are shifted by about 15 $cm^{-1}$ to higher wavenumbers compared to those of the corresponding aryl precursors. This is likely due to a reduction of electron density on chromium metal consistent with the introduction of an electron-withdrawing functionality between the aromatic cycle and palladium.[21]

The $^{31}P\{^1H\}$ NMR spectra of complexes **8–12** present only one singlet; this still suggests a trans configuration for monomeric complexes **8–10**; for dimeric complexes **11** and **12**, the equivalence of the phosphorus atoms also indicates that two CO molecules have been inserted in the two $\sigma$-aryl bonds.

**2. Cleavage of Cl Bridges and Exchange of Phosphine in Complex 11.** The aroyl complex **13** could be prepared quantitatively by treatment of **11** with 2 equiv of dppe (eq 7).

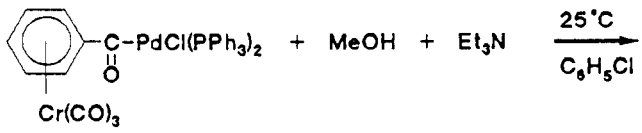



Complex **13** exhibits a band at 1642 $cm^{-1}$ in its infrared spectrum assigned to the acyl group. The $^{31}P\{^1H\}$ NMR spectrum presents two doublets centered at 42.8 and 26.37 ppm with a coupling constant of 42 Hz suggesting a cis configuration of the molecule.

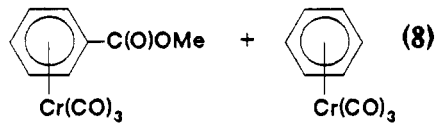
**C. Reaction of Complexes 8 and 11 with Methanol and Triethylamine.** When complex **8** in chlorobenzene solution is allowed to react at room temperature with an excess of methanol, no reaction is observed even after 2 h. However when an excess of triethylamine is added to the previous solution, a rapid formation of tricarbonyl(methylbenzoate)chromium is observed by GLC, accompanied by small amounts of tricarbonyl(benzene)chromium (eq 8).

The dimeric complex **11** reacts similarly with methanol and triethylamine to produce the chromium-containing ester (Scheme II, path k).

As in previous mechanistic studies,[13] the formation of an acyl(alkoxy)palladium complex $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3](OMe)(PPh_3)_y\}_{2/y}$ between $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr$-




8




85% 15%

$(CO)_3]Cl(PPh_3)_y\}_{2/y}$ and the carbonylation product $(\eta^6$-$C_6H_5COOMe)Cr(CO)_3$ could not be observed; this suggests that the final reductive elimination between the acyl and methoxy ligands is more rapid than the substitution of chlorine by the methoxy group.

## Discussion

A series of bimetallic complexes with various phosphine ligands has been prepared, which are assumed to be possible intermediates in the catalytic carbonylation of tricarbonyl(chlorobenzene)chromium. These preparations have been transposed from the mechanism proposed by Yamamoto et al.[13] for the alkoxycarbonylation of iodobenzene. Thus (a) monomeric and dimeric complexes of the type $\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Cl)L_y\}_{2/y}$ were first obtained, (b) monomeric and dimeric complexes of the type $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3](Cl)L_y\}_{2/y}$ were formed by CO insertion into the $\sigma$-aryl–Pd bond of the former complexes, (c) tricarbonyl(methylbenzoate)chromium was finally obtained by methanolysis, in the presence of triethylamine, of monomeric and dimeric complexes of the latter type with $PPh_3$ ligand.

This illustrates the possibility of achieving the methoxycarbonylation of tricarbonyl(chlorobenzene)chromium via these aryl- and aroyl-type palladium complexes and makes them credible reaction intermediates. This also shows that the $Cr(CO)_3$ group remains coordinated, at room temperature, to the various intermediates throughout the catalytic cycle; this was also observed during the catalytic reaction performed at 100 °C.[9]

Up to now, all the reported mechanisms of palladium-catalyzed carbonylation of aryl halides involved monomeric intermediates; the present study shows that dimeric species can also participate in the catalytic cycle (Scheme III).

We would like to focus on the role of the $Cr(CO)_3$ moiety in each of these steps. In regards to the oxidative addition of aryl halides to $Pd(PPh_3)_4$ PhX + $Pd(PPh_3)_4$ → $PhPdX(PPh_3)_2$ + $2PPh_3$ (X = Cl, Br, I), it is known to occur respectively at 140 and 80 °C and room temperature when X is Cl,[19,20] Br,[33] or I[34]. In the case of aryl chlorides, Fitton and Rick have reported that this reaction can proceed between 80 and 100 °C when electron-withdrawing substituents are present on the aromatic ring.[33] When the $Cr(CO)_3$ moiety is coordinated to chlorobenzene, we have observed that oxidative addition can be performed at room temperature. The same reason can be put forward in both cases since the $Cr(CO)_3$ group is known to exert a strong electron-withdrawing effect.[11] With zerovalent palladium complexes, oxidative addition of PhX is often compared to a nucleophilic attack of the palladium center on the ipso carbon.[6] Thus, lowering the electron density of the aromatic ring in chlorobenzene is reasonably expected to favor this elementary step.

Obviously, other parameters have been shown to play a role in the oxidative addition step:[7,8] (a) the degree of coordinative unsaturation of the palladium, which can be controlled by the steric constraints of the ligands; (b) the nucleophilic character of palladium, which is influenced by the basicity of the ligands.

In our case, the fact that oxidative addition occurs easily at room temperature with $Pd(PPh_3)_4$ or $Pd(dba)_2$ + $xL$ does not necessarily mean that during a catalytic reaction, this step proceeds so easily. Let us recall that the catalytic methoxycarbonylation of $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$ requires a temperature of 80 °C to proceed at a significant rate. The presence of CO probably modifies the nature of the active palladium species, the degree of its unsaturation (formation of $Pd(CO)_nL_m$ species), and also the nucleophilic character of palladium. As an illustration of this inhibiting role of CO in the crucial step of oxidative addition, we have observed that the so-called Heck reaction between chlorobenzene and styrene, PhCl + Ph—CH=$CH_2$ → Ph—CH=CH—Ph + HCl, which proceeds via an oxidative addition of chlorobenzene to a zerovalent $Pd(PPh_3)_x$ complex,[35,36] is completely inhibited by the presence of a CO atmosphere of 3 bar.

In regards to the insertion of CO into the $\sigma$-aryl–Pd bond, it generally occurs easily at room temperature under 1 bar of CO with the monomeric and dimeric complexes (except the cases of **3** (L = $PCy_3$) and **6** ($L_2$ = dppe)). Although we have not carried out kinetic studies of this elementary step, the rate of reaction is quite high at room temperature and is qualitatively comparable to that observed by Heck with analogous compounds without chromium.[14] The presence of the $Cr(CO)_3$ moiety, at least in a first approximation, does not drastically slow down this step, as one would expect from the Heck results: electron-withdrawing substituents on the aromatic ring were shown to decrease the rate of CO insertion.[14]

Conversely, a significant ligand effect is observed on this CO insertion step; in the case of the dimeric complex **3** with $PCy_3$, 5 bar of CO is necessary to observe the reaction, and with complex **6** (L = dppe), the reaction does not proceed even under 30 bar of CO. The limiting effect of basic phosphines has already been mentioned by Anderson for analogous dimeric palladium complexes.[26] It may be due to the equilibrium of the phosphine dissociation itself or more likely to the equilibrium of the Cl-bridge opening, which can be phosphine dependent; indeed, in the case of dimeric platinum complexes, Cl-bridge cleavage by CO occurs, but no CO insertion is observed. Two monomeric carbonyl complexes are then formed:[37]


This suggests that carbonylation of dimers **2** and **3** should proceed similarly via the Cl-bridge cleavage or possibly via a rapid equilbration of the dimer to a monomer in order to liberate a coordination site for CO; these processes would be more difficult in the case of basic ligand like $PCy_3$.

(33) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.
(34) Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6.
(35) Julia, M.; Duteil, M.; Grard, C.; Kuntz, E. *Bull. Soc. Chim. Fr.* **1973**, 2731.
(36) Davison, J. B.; Simon, N. M.; Sojka, S. A. *J. Mol. Catal.* **1984**, *22*, 349.
(37) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1434.

**Table VI. NMR and IR Data for Complexes $\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Cl)L_y\}_{2/y}$ and $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3](Cl)L_y\}_{2/y}$[a]**

| complex (L) | $^{13}C\{^1H\}$ NMR,[b] ppm | $^1H$ NMR,[c] ppm | assignt | $^{31}P\{^1H\}$ NMR,[d] ppm | IR[e] $\nu$(CO), cm$^{-1}$ | assignt |
|---|---|---|---|---|---|---|
| 1 ($PPh_3$) | | 7.2–7.9 (m) | $C_6H_5$ | 25.4 | 1947, 1867 | $Cr(CO)_3$ |
| | 235 | | $Cr(CO)_3$ | | | |
| 2 ($PPh_3$) | 87.9–101.8 | 4.43–5.56 | $(\eta^6\text{-}C_6H_5)Cr$ | 35.32 | 1947, 1867 | $Cr(CO)_3$ |
| | 128.7–135.5 | 7.30–7.61 | $P(C_6H_5)_3$ | | | |
| | 235.6 | | $Cr(CO)_3$ | | | |
| 3 ($PCy_3$) | | | | 36.88 | 1953, 1882, 1860 | $Cr(CO)_3$ |
| 4 ($PPhEt_2$) | 8.27 | 0.7–1.2 | $CH_3$ | 15.24 | 1945, 1858, 1840 | $Cr(CO)_3$ |
| | 14.8–15.9 | 2.03–2.20 | $CH_2$ | | | |
| | 91–105.4 | 4.65–6.75 | $(\eta^6\text{-}C_6H_5)Cr$ | | | |
| | 127.66–138.9 | 7.18–7.55 | $P(C_6H_5)$ | | | |
| | 235.9 | | $Cr(CO)_3$ | | | |
| 5 ($PPh_2Et$) | | | | 21.67 | 1940, 1860, 1840 | $Cr(CO)_3$ |
| 6 (dppe)[f] | 20–30 | 1.83–2.74 | $CH_2$ | 59.7 (d) | 1940, 1860, 1822 | $Cr(CO)_3$ |
| | 92.8–105.2 | 4.67–5.38 | $(\eta^6\text{-}C_6H_5)Cr$ | 42.7 (d) | | |
| | 116–134.5 | 7.30–7.85 | $P(C_6H_5)_2$ | $J_{P-P}$ = 23 Hz | | |
| | 236.54 | | $Cr(CO)_3$ | | | |
| 7 (dpph)[g] | | | | 19.51 | 1950, 1860 | $Cr(CO)_3$ |
| 8 ($PPh_3$) | | | | 21.53 | 1972, 1894 | $Cr(CO)_3$ |
| | | | | | 1650 | acyl |
| 9 ($PEt_2Ph$) | 8 | 0.81–1.27 | $CH_3$ | 11.98 | 1972, 1910, 1890 | $Cr(CO)_3$ |
| | 14.36–16.53 | 1.84–2.28 | $CH_2$ | | 1640 | acyl |
| | 89.85–105 | 4.89–5.70 | $(\eta^6\text{-}C_6H_5)Cr$ | | | |
| | 128.7–132.2 | 7.29–7.58 | $P(C_6H_5)$ | | | |
| | 231 | | C=O acyl | | | |
| | 232.2 | | $Cr(CO)_3$ | | | |
| 10 (dpph)[g] | | | | 14.64 | 1967, 1890 | $Cr(CO)_3$ |
| | | | | | 1639 | acyl |
| 11 ($PPh_3$) | | | | 27.06 | 1980, 1925, 1890 | $Cr(CO)_3$ |
| | | | | | 1657 | acyl |
| 12 ($PCy_3$) | 10.2–35.76 | | $P(C_6H_{11})_3$ | 39.76 | 1980, 1922, 1907 | $Cr(CO)_3$ |
| | 90–103 | | $(\eta^6\text{-}C_6H_5)Cr$ | | 1650 | acyl |
| | 217.35 | | C=O acyl | | | |
| | 232 | | $Cr(CO)_3$ | | | |
| 13 (dppe)[f] | 20–30 | 1.93–2.85 | $CH_2$ | 42.8 (d) | 1960, 1900, 1870 | $Cr(CO)_3$ |
| | 89.9–108.6 | 4.61–5.87 | $(\eta^6\text{-}C_6H_5)Cr$ | 26.37 (d) | 1642 | acyl |
| | 128.2–139.3 | 7.03–8.02 | $P(C_6H_5)_2$ | $J_{P-P}$ = 42 Hz | | |
| | 232.45 | | $Cr(CO)_3$ | | | |
| | 233.9 | | C=O acyl | | | |

[a] Dimers when $y = 1$, monomers when $y = 2$. [b] At 25 MHz in acetone-$d_6$ (1) or $CD_2Cl_2$ (2–13), at 25 °C. [c] At 100 MHz in acetone-$d_6$ (1) or $CD_2Cl_2$ (2–13), at 25 °C. [d] At 81 MHz in $C_6D_6$ except 8 ($CDCl_3$) and 9, 10, 13 ($CD_2Cl_2$), at 25 °C. [e] In KBr disks. [f] dppe = bis(diphenylphosphine)ethane. [g] dpph = bis(diphenylphosphine)hexane.

Similarly, the nonreactivity of the monomeric complex **6** with dppe ligand toward CO insertion is probably due to the strong chelating effect of this ligand, which prevents its dissociation and, therefore, CO coordination.

Methanolysis of the acyl derivatives has not been fully explored. It is probably a multistep process, but no intermediates could be identified. As for the preceding CO insertion step, the presence of the $Cr(CO)_3$ moiety does not seem to influence notably the kinetics of this reaction compared to analogous chromium-free acyl intermediates.[13,14,17]

## Conclusion

This study has shown that monomeric and dimeric complexes of the type $\{Pd[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Cl)L_y\}_{2/y}$ and $\{Pd[(\eta^6\text{-}C_6H_5CO)Cr(CO)_3](Cl)L_y\}_{2/y}$ are intermediates in the stoichiometric transformation at room temperature of tricarbonyl(chlorobenzene)chromium to tricarbonyl(methyl benzoate) chromium and can be reasonably considered as intermediates in the catalytic methoxycarbonylation of $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$; for the first time, dimeric species are assumed to participate in catalytic carbonylation reactions.

This study also enlightens the crucial promoting effect of the electron-withdrawing $Cr(CO)_3$ moiety on the oxidative addition of the C–Cl bond of chloroaromatics to zerovalent palladium species; during this step, a bimetallic activation of the aromatic substrate is performed via a $\sigma$-coordination to palladium and a $\pi$-coordination to chromium.

## Experimental Section

All manipulations of the complexes were carried out under argon and sheltered from full light. Before use, the solvents were dried, distilled, and deoxygenated according to usual methods. $PdCl_2$ was purchased from Johnson Matthey, $Cr(CO)_6$ from Strem Chemicals, dba and all the phosphine ligands from Aldrich, and the silanized silica gel from Merck.

$Pd(PPh_3)_4$[38] and $Pd(dba)_2$[39] were prepared from $PdCl_2$ and $(\eta^6\text{-}C_5H_5Cl)Cr(CO)_3$[40] was prepared from $Cr(CO)_6$ according to literature methods. The elemental analyses were carried out by the Pascher Laboratory (FRG). IR spectra of complexes in KBr matrix were recorded on a FT Nicolet 10 Mx spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Brücker AC 100 and $^{31}P$ NMR spectra on a Brücker 200 spectrometer. Chemical shifts are expressed relative to TMS for $^1H$ and $^{13}C$ and to 85% $H_3PO_4$ for $^{31}P$.

**Crystal Structure Determination and Refinement.** Intensity data for complexes **3** and **6** were collected on an Enraf-Nonius CAD 4 diffractometer with Mo K$\alpha$ radiation. Compound **3** crystallizes in the orthorhombic system, in space group *Pccm* with the parameters $a$ = 18.486 (8) Å, $b$ = 20.401 (7) Å, and $c$ = 17.255 (7) Å. The unit cell parameters were obtained by solution and refinement of the angular settings from 25 reflections well distributed in the measurement zone. No intensity degradation was observed during the data collection. All data were corrected for Lorentz and polarization effects as well as for absorption by the DIFABS program.[41] Calculations were carried out with the

(38) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(39) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
(40) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

program CRYSTALS[42] on an Alliant VFX80 computer. All atoms were localized by direct methods, followed by calculations of atomic structure factors and difference Fourier techniques. A molecule of deuterated benzene was observed in the unit cell; because of the great thermal agitation of its atoms, only an isotropic refinement of this molecule was performed. All the other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on a Fourier difference map and then placed at a distance of 0.97 Å from the atom to which they are bonded; the thermal agitation for the hydrogen atoms was fixed at 1.1 times the value of their bearing atoms. They were introduced in the structure factor calculation but not refined. According to the secondary extinction and the anormal diffusion, an $R$ factor of 0.0416 was finally obtained.

Complex **6** crystallizes in the monoclinic system, in space group $P2_1/n$ with the parameters $a$ = 9.841 (2) Å, $b$ = 12.783 (5) Å, $c$ = 28.377 (2) Å, and $\beta$ = 92.23 (1)°. The structure was solved by standard Patterson–Fourier techniques from 4031 unique observed reflections and refined by least-squares procedures for 499 variables to $R$ = 0.0373, $R_w$ = 0.0405. Hydrogen atoms were located on a difference Fourier map and refined with an overall isotropic temperature factor. All non-hydrogen atoms were refined anisotropically, except the Cl atoms of a disordered solvent molecule ($CH_2Cl_2$).

**Preparation of *trans*-Pd[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]Cl(PPh$_3$)$_2$ (1). (a) Starting from Pd(PPh$_3$)$_4$.** A solution of $Pd(PPh_3)_4$ (6 g, 5.19 mmol) and ($\eta^6$-$C_6H_5Cl$)$Cr(CO)_3$ (1.3 g, 5.19 mmol) in freshly distilled and dried toluene (40 mL) was stirred at room temperature for 18 h. The solution, initially a cloudy yellow, changed slowly to become a cloudy orange. After evaporation of solvent, the solid obtained was washed with $Et_2O$ (5 × 10 mL) in order to remove excess $PPh_3$ and then dried under vacuum to give a yellow powder: 4.3 g; 94%.

**(b) Starting from Pd(dba)$_2$.** A solution of ($\eta^6$-$C_6H_5Cl$)$Cr(CO)_3$ (348 mg, 1.4 mmol) in toluene (5 mL) was added drop by drop at room temperature to a solution of $Pd(dba)_2$ (808 mg, 1.4 mmol) and $PPh_3$ (1.1 g, 4.2 mmol) in toluene (10 mL). This mixture was stirred for 5 h. After evaporation of the solvent, the resulting green-brown solid was washed with $Et_2O$ (5 × 10 mL) in order to remove the dba released during the reaction and excess phosphine. The solid was then dissolved in THF (5 mL), and the solution was filtered to remove any traces of metallic palladium. Evaporation of the solvent led to a yellow-brown solid: 990 mg; 80%.

With both preparation methods, $^{31}P\{^1H\}$ NMR spectra indicated that the final product was a mixture. Isolation of complex **1** was obtained by liquid chromatography (benzene/silated silica, argon atmosphere) with a 70% yield with respect to the crude product.

Anal. Calcd for $C_{45}H_{35}ClCrO_3P_2Pd$: C, 61.4; H, 4.00; Cl, 4.03; Cr, 5.91; O, 5.46; P, 7.05; Pd, 12.1. Found: C, 61.05; H, 4.21; Cl, 4.12; Cr, 6.14; O, 5.30; P, 6,65; Pd, 12.53. IR (KBr): $\nu$(CO) 1947, 1867 cm$^{-1}$; $\nu$(C=C) 1480, 1440 cm$^{-1}$; $\delta$(C=C) 745, 695 cm$^{-1}$. $^1H$ NMR (100 MHz, $(CD_3)_2CO$, ppm): 7.2–7.9 (m). $^{13}C\{^1H\}$ NMR (25 MHz, $(CD_3)_2CO$, ppm): 235 ($Cr(CO)_3$, s). $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 25.4 (s).

**Preparation of Pd$_2$[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]$_2$($\mu$-Cl)$_2$(PPh$_3$)$_2$ (2).** A yellow solution of $Pd(dba)_2$ (1.15 g, 2 mmol), ($\eta^6$-$C_6H_5Cl$)$Cr(CO)_3$ (645 mg, 2.6 mmol), and $PPh_3$ (815 mg, 3.1 mmol) in benzene (20 mL) was stirred at room temperature for 18 h, during which time a brown precipitate was formed. After evaporation of the solvent, the resulting solid was washed with $Et_2O$ (4 × 20 mL) to remove the dba released during the reaction and excess phosphine. The brown solid was then dissolved in THF (10 mL) and filtered to remove traces of metallic palladium. After evaporation of the solvent, the solid crystallized from acetone at −20 °C in the form of orange needles: 600 mg; 48%.

Anal. Calcd for $C_{54}H_{40}Cl_2Cr_2O_6P_2Pd_2$: C, 52.52; H, 3.24; Cr, 8.43; Pd, 17.24. Found: C, 52.11; H, 3.15; Cr, 8.19; Pd, 17.63. IR (KBr): $\nu$(CO) 1947, 1867 cm$^{-1}$; $\nu$(C=C) 1480, 1438 cm$^{-1}$. $^1H$ NMR (100 MHz, $CD_2Cl_2$, ppm): 4.43–5.56 (($\eta^6$-$C_6H_5$)$Cr(CO)_3$, m, 10 H), 7.30–7.61 ($P(C_6H_5)_3$, m, 30 H). $^{13}C\{^1H\}$ NMR (25 MHz, $CD_2Cl_2$, ppm): 87.9–101.8 (($\eta^6$-$C_6H_5$)Cr, m), 128.7–135.5 ($P(C_6H_5)_3$, m), 235.6 ($Cr(CO)_3$, s). $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 35.32 (s).

**Preparation of Pd$_2$[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]$_2$($\mu$-Cl)$_2$(PCy$_3$)$_2$ (3).** A green solution of $Pd(dba)_2$ (575 mg, 1 mmol), ($\eta^6$-$C_6H_5Cl$)$Cr(CO)_3$ (298 mg, 1.2 mmol), and $PCy_3$ (560 mg, 2 mmol) in benzene (20 mL) was stirred at room temperature for 18 h, during which time a green precipitate was formed. After evaporation of the solvent, the solid was washed with $Et_2O$ (4 × 10 mL); it was then dissolved in benzene, filtered on silated silica, and precipitated by hexane after concentration to give yellow crystals: 400 mg; 63%.

Anal. Calcd for $C_{54}H_{76}Cl_2Cr_2O_6P_2Pd_2$: C, 51.02; H, 6.0; Cr, 8.18; Pd, 16.75. Found: C, 50.65; H, 6.14; Cr, 7.85; Pd, 17.19. IR (KBr): $\nu$(CO) 1953, 1882, 1860 cm$^{-1}$; $\nu$(C=C) 1480 cm$^{-1}$. $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 36.88 (s).

**Preparation of *trans*-Pd[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]Cl(PEt$_2$Ph)$_2$ (4) and *trans*-Pd[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]Cl(PPh$_2$Et)$_2$ (5).** A solution of Pd$_2$[($\eta^6$-$C_6H_5$)$Cr(CO)_3$]$_2$($\mu$-Cl)$_2$($PPh_3$)$_2$ (**2**) (330 mg, 0.266 mmol) and $PEt_2Ph$ (200 μL, 1.11 mmol) in benzene (7 mL) was stirred at room temperature for 30 min. After evaporation of the solvent, the green solid was dissolved in $Et_2O$ (5 mL) and the solution was filtered on silated silica. After concentration, a yellow solid was precipitated by hexane (10 mL), washed further with hexane, and dried in vacuo: 300 mg, 81%.

Anal. Calcd for $C_{29}H_{35}ClCrO_3P_2Pd$: C, 50.66; H, 5.09; Cl, 5.17; Cr, 7.57; O, 6.98; P, 9.02; Pd, 15.48. Found: C, 51.16; H, 5.21; Cl, 5.18; Cr, 7.22; O, 7.03; P, 9.11; Pd, 15.3. IR (KBr): $\nu$(CO) 1945, 1858, 1840 cm$^{-1}$; $\nu$(C=C) 1480, 1440 cm$^{-1}$. $^1H$ NMR (100 MHz, $CD_2Cl_2$, ppm); 0.7–1.2 ($CH_3$, m, 12 H), 2.03–2.20 ($CH_2$, m, 8 H), 4.65–6.75 (($\eta^6$-$C_6H_5$)$Cr(CO)_3$, m, 5 H), 7.18–7.55 ($P(C_6H_5)$, m, 10 H). $^{13}C\{^1H\}$ NMR (25 MHz, $CD_2Cl_2$, ppm): 8.27 ($CH_3$, s), 14.8–15.9 ($CH_2$, t), 91–105.4 (($\eta^6$-$C_6H_5$)Cr, m), 127.66–138.9 ($P(C_6H_5)$, m), 235.9 ($Cr(CO)_3$, s). $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 15.24 (s).

Complex **5** was prepared analogously.

**Preparation of *cis*-Pd[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]Cl(dppe) (6) and *trans*-Pd[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]Cl(dpph) (7).** A green solution of Pd$_2$[($\eta^6$-$C_6H_5$)$Cr(CO)_3$]($\mu$-Cl)$_2$($PPh_3$)$_2$ (**2**) (494 mg, 0.4 mmol) and dppe (350 mg, 0.88 mmol) in benzene (5 mL) was stirred at room temperature for 30 min. A green solid was precipitated by hexane (10 mL), filtered, washed with hexane (5 mL), and dried in vacuo: 600 mg, 100%. The product was recrystallized from $CH_2Cl_2$/hexane.

Anal. Calcd for $C_{35}H_{29}ClCrO_3P_2Pd$: C, 55.80; H, 3.88; Cl, 4.70; Cr, 6.90; O, 6.37; P, 8.22; Pd, 14.12. Found: C, 56.21; H, 4.18; Cl, 4.36; Cr, 6.24; O, 5.97; P, 7.68; Pd, 13.55. IR (KBr): $\nu$(CO) 1940, 1860, 1822 cm$^{-1}$; $\nu$(C=C) 1480, 1440 cm$^{-1}$. $^1H$ NMR (100 MHz, $CD_2Cl_2$, ppm): 1.83–2.74 ($CH_2$, m, 4 H), 4.67–5.38 (($\eta^6$-$C_6H_5$)$Cr(CO)_3$, m, 5 H), 7.30–7.85 ($P(C_6H_5)_2$, m, 20 H). $^{13}C\{^1H\}$ NMR (25 MHz, $CD_2Cl_2$, ppm): 20–30 ($CH_2$, m), 92.8–105.2 (($\eta^6$-$C_6H_5$)Cr, m), 116–134.5 ($P(C_6H_5)_2$, m), 236.54 ($Cr(CO)_3$, s). $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 59.7 (d, $^2J_{P-P}$ = 22.9 Hz), 42.7 (d, $^2J_{P-P}$ = 23 Hz).

Complex **7** was prepared analogously.

Anal. Calcd for $C_{39}H_{37}ClCrO_3P_2Pd$: C, 57.86; H, 4.61; Cl, 4.38; Cr, 6.42; O, 5.93; P, 7.65; Pd, 13.14. Found: C, 57.53; H, 4.82; Cl, 4.21; Cr, 5.78; O, 5.62; P, 7.25; Pd, 13.61. IR (KBr): $\nu$(CO) 1950, 1860 cm$^{-1}$; $\nu$(C=C) 1480, 1440 cm$^{-1}$. $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 19.51 (s).

**Preparation of Complexes {Pd[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]-(Cl)L$_y$}$_{2/y}$ (8–11).** CO was bubbled through a solution of complexes **1**, **2**, **4**, or **7** (1 mmol) in benzene (6 mL) at room temperature for 2 h. After concentration, hexane was added until a solid precipitated, which was filtered, washed with hexane (5 mL), and dried in vacuo. Yields: **8**, 85%; **9**, 80%; **10**, 90%; **11**, 100%.

**8: *trans*-Pd[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]Cl(PPh$_3$)$_2$.** IR (KBr): $\nu$(CO) 1972, 1894 cm$^{-1}$; $\nu$(C=O) 1650 cm$^{-1}$. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, ppm): 21.53 (s).

**9: *trans*-Pd[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]Cl(PEt$_2$Ph)$_2$.** IR (KBr): $\nu$(CO) 1972, 1910, 1890 cm$^{-1}$; $\nu$(C=O) 1640 cm$^{-1}$. $^1H$ NMR (100 MHz, $CD_2Cl_2$, ppm): 0.81–1.27 ($CH_3$, m, 12 H), 1.84–2.28 ($CH_2$, m, 8 H), 4.89–5.70 (($\eta^6$-$C_6H_5CO$)$Cr(CO)_3$, m, 5 H), 7.29–7.58 ($P(C_6H_5)$, m, 10 H). $^{13}C\{^1H\}$ NMR (25 MHz, $CD_2Cl_2$, ppm): 8 ($CH_3$, s), 14.36–16.53 ($CH_2$, m), 89.85–105 (($\eta^6$-$C_6H_5$)Cr, m) 128.7–132.2 ($P(C_6H_5)$, m) 231 (C=O acyl, s), 232.2 ($Cr(CO)_3$, s). $^{31}P\{^1H\}$ NMR

(41) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.
(42) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1986.

(81 MHz, $CD_2Cl_2$, ppm): 11.98 (s).

**10: *trans*-Pd[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]Cl(dpph).** IR (KBr): $\nu$(CO) 1967, 1890 cm$^{-1}$; $\nu$(C=O) 1639 cm$^{-1}$. $^{31}P\{^1H\}$ NMR (81 MHz, $CD_2Cl_2$, ppm): 14.64 (s).

**11: Pd$_2$[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]$_2$($\mu$-Cl)$_2$(PPh$_3$)$_2$.** Anal. Calcd for $C_{56}H_{40}Cl_2Cr_2O_8P_2Pd_2$: C, 52.12; H, 3.12; Cl, 5.49; Cr, 8.06; O, 9.92; P, 4.80; Pd, 16.49. Found: C, 52.61; H, 3.42; Cl, 5.07; Cr, 7.44; O, 9.38; P, 4.45; Pd, 16.75. IR (KBr): $\nu$(CO) 1980, 1925, 1890 cm$^{-1}$; $\nu$(C=O) 1657 cm$^{-1}$; $\nu$(C=C) 1480, 1438 cm$^{-1}$. $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 27.06 (s).

**Preparation of Pd$_2$[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]$_2$($\mu$-Cl)$_2$(PCy$_3$)$_2$ (12).** A solution of Pd$_2$[($\eta^6$-$C_6H_5$)Cr(CO)$_3$]$_2$($\mu$-Cl)$_2$(PCy$_3$)$_2$ (3) (508 mg, 0.4 mmol) in benzene (7 mL) was charged in a stainless steel reactor under 5 bar of CO and stirred overnight at room temperature. The green-brown solid formed was filtered, washed with hexane (5 mL), and dried in vacuo: 530 mg, 100%.

Anal. Calcd for $C_{56}H_{76}Cl_2Cr_2O_8P_2Pd_2$: C, 50.67; H, 5.73; Cr, 7.84; Pd, 16.04. Found: C, 50.28; H, 5.89; Cr, 7.42; Pd, 16.59. IR (KBr): $\nu$(CO) 1980, 1922, 1907 cm$^{-1}$; $\nu$(C=O), 1650 cm$^{-1}$. $^{13}C\{^1H\}$ NMR (25 MHz, $CD_2Cl_2$, ppm): 10.2–35.76 (P($C_6H_{11}$)$_3$, m), 90–103 (($\eta^6$-$C_6H_5$)Cr, m), 217.35 (C=O acyl, s), 232 (Cr(CO)$_3$, s). $^{31}P\{^1H\}$ NMR (81 MHz, $C_6D_6$, ppm): 39.76 (s).

**Preparation of *cis*-Pd[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]Cl(dppe) (13).** A dark green solution of Pd$_2$[($\eta^6$-$C_6H_5CO$)Cr(CO)$_3$]$_2$($\mu$-Cl)$_2$(PPh$_3$)$_2$ (516 mg, 0.4 mmol) and dppe (350 mg, 0.88 mmol) in benzene (5 ml) was stirred at room temperature for 1 h. A light green solid was precipitated by hexane (10 mL), filtered off, washed further with hexane (5 mL), and dried in vacuo: 610 mg, 97%.

Anal. Calcd for $C_{36}H_{29}ClCrO_4P_2Pd$: C, 55.32; H, 3.71; Cr, 6.65; Pd, 13.62. Found: C, 55.69; H, 3.98; Cr, 6.18; Pd, 14.02. IR (KBr): $\nu$(CO) 1960, 1900, 1870 cm$^{-1}$; $\nu$(C=O) 1462 cm$^{-1}$; $\nu$(C=C) 1480, 1440 cm$^{-1}$. $^1H$ NMR (100 MHz, $CD_2Cl_2$, ppm): 1.93–2.85 ($CH_2$, m, 4 H), 4.61–5.87 (($\eta^6$-$C_6H_5$)Cr(CO)$_3$, m, 5 H), 7.03–8.02 (P($C_6H_5$)$_2$, m, 20 H). $^{13}C\{^1H\}$ NMR (25 MHz, $CD_2Cl_2$, ppm) 20–30 ($CH_2$, m), 89.9–108.6 ($\eta^6$-$C_6H_5$)Cr, m), 128.2–139.3 (P($C_6H_5$)$_2$, m), 232.45 (Cr(CO)$_3$, s), 233.9 (C=O acyl, s). $^{31}P\{^1H\}$ NMR (81 MHz, $CD_2Cl_2$, ppm): 42.8 (d, $^2J_{P-P}$ = 42 Hz), 26.37 (d, $^2J_{P-P}$ = 42 Hz).

**Reaction of Complexes 8 and 11 with Methanol and Triethylamine.** Triethylamine (140 $\mu$L, 1 mmol) was added dropwise to a stirred solution of 8 (363 mg, 0.4 mmol) or 11 (258 mg, 0.2 mmol) in chlorobenzene (19 mL), methanol (1 mL), and dodecane (500 $\mu$L, internal standard for GLC). The clear solution darkened instantaneously. The products were analyzed by GLC on a 25 m Cp sil 5 capillary column.

**Registry No.** 1, 136805-06-6; 2, 136827-07-1; 3, 136805-07-7; 4, 136805-08-8; 5, 136805-09-9; 6, 136805-10-2; 7, 136827-08-2; 8, 136805-11-3; 9, 136805-12-4; 10, 136805-13-5; 11, 136805-14-6; 12, 136805-15-7; 13, 136805-16-8; ($\eta^6$-$C_6H_5Cl$)Cr(CO)$_3$, 12082-03-0; Pd(PPh$_3$)$_4$, 14221-01-3.

**Supplementary Material Available:** Tables of crystal data, hydrogen fractional coordinates and thermal parameters, anisotropic thermal parameters, and bond lengths and bond angles for 3 and 6 (10 pages); listings of structure factors for 3 and 6 (31 pages). Ordering information is given on any current masthead page.

# Ligand Effects on the Rates of the Migratory Insertion in Rhodium(III) Methyl Carbonyl Complexes

Donato Monti and Mauro Bassetti*

*Centro CNR di Studio sui Meccanismi di Reazione, Dipartimento di Chimica, Università "La Sapienza", P. le Aldo Moro 2, 00185 Roma, Italy*

Glenn J. Sunley, Paul Ellis, and Peter Maitlis*

*Department of Chemistry, The University, Sheffield S3 7HF, England*

*Received April 18, 1991*

The complexes ($\eta^5$-$C_5Me_5$)Rh(CO)(X)(Me) (X = I, Br, Cl, $MeCO_2$, $CF_3CO_2$) react readily with triphenylphosphine in toluene at 25 °C to yield quantitatively the corresponding acyl species ($\eta^5$-$C_5Me_5$)Rh(COMe)(X)(PPh$_3$). The reactions of the halide complexes are first order in both the substrate and the phosphine. The rate increases in the order I < Br < Cl, following the increasing electronegativity of the halogen atoms. The activation parameters ($\Delta H^\ddagger$ = 56 ± 2 (I), 46 ± 3 (Br), 36 ± 2 (Cl) kJ mol$^{-1}$; $\Delta S^\ddagger$ = −79 ± 4 (I), −93 ± 5 (Br), −122 ± 3 (Cl) J K$^{-1}$ mol$^{-1}$) indicate that the order of reactivity is dominated by changes in $\Delta H^\ddagger$. The carboxylate complexes exhibit saturation kinetics, typical of the formation of an intermediate and unprecedented for migratory insertion in a nonpolar solvent. It is proposed that the intermediate is ($\eta^5$-$C_5Me_5$)Rh($\eta^2$-$O_2CR$)(COMe) (R = Me, $CF_3$), where the carboxylate moiety acts as a bidentate ligand to stabilize the otherwise unsaturated species. The rate constant for the formation of the intermediate, determined from the reactions with different nucleophiles, is somewhat larger for X = $CF_3CO_2$ ($k_1$ = 0.16 s$^{-1}$) than for X = $MeCO_2$ ($k_1$ = 0.105 s$^{-1}$).

## Introduction

The migratory insertion of carbon monoxide into metal–alkyl bonds is a reaction of fundamental importance in organometallic chemistry and has extensive application in catalysis.[1] Many features of this reaction, including kinetics and mechanism,[2] stereochemistry,[3] migratory aptitudes of alkyl and aryl groups,[4,5] the influence of solvents

(1) (a) Collman, J. A.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Kuhlman, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (c) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(2) (a) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994. (b) Butler, I. S.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074. (c) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345.

(3) (a) Calderazzo, F.; Noack, K. *J. Organomet. Chem.* **1967**, *10*, 101. (b) Brunner, H.; Hammer, B.; Bernal, I.; Draux, M. *Organometallics* **1983**, *2*, 1595. (c) Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* **1984**, *106*, 2853. (d) Wright, S. C.; Baird, M. C. *J. Am. Chem. Soc.* **1985**, *107*, 6899.

0276-7333/91/2310-4015$02.50/0 