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Reaction of CO with a Methylpalladium Heterocyclic Carbene Complex: Product Decomposition Routes—Implications for Catalytic Carbonylation Processes

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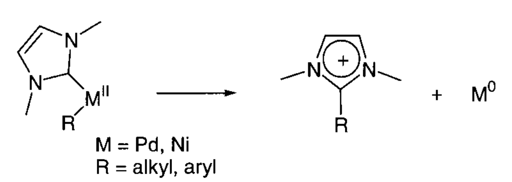
Summary: The methylpalladium−heterocyclic carbene dimer $[PdMe(tmiy)(\mu\text{-}Cl)]_2$ ***(1)*** *(tmiy = 1,3,4,5-tetramethylimidazolin-2-ylidene) reacts with CO to yield [PdMeCl(tmiy)CO] (**2**) through cleavage of the Cl bridge. Complex **2** decomposes in solution to yield the 1,2,3,4,5-pentamethylimidazolium ion (**I**) along with a small amount of 2-acyl-1,3,4,5-tetramethylimidazolium (**II**). In the presence of* $AgBF_4$ *the dimer reacts with CO to give **II** as the major product. The reaction sequence is interpreted as evidence for CO insertion into the Pd−Me bond of **2** and also represents a possible mode of deactivation for potential CO/ethylene copolymerization catalysts based on heterocylic carbene complexes.*

Introduction

Heterocyclic carbene complexes of transition metals have recently been reported to act as precatalysts for a variety of reactions, and there has been considerable excitement regarding the potential of these new species.[1−14] However, in two recent reports[9,10] we have shown that alkyl and aryl Pd^{II} and Ni^{II} heterocyclic carbene complexes readily decompose via elimination of hydrocarbyl imidazolium salts, directly affording zerovalent Pd or Ni (reaction 1). With cationic complexes decomposition is often more facile, and in a number of complexes the decomposition occurs rapidly even at low temperature. As hydrocarbylmetal complexes are expected to be intermediates in many catalytic reactions, including those for which Pd and Ni carbene complexes have been applied,[10,14] this mode of decomposition represents a disturbing route to catalyst deactivation. In keeping with this concern it is only very recently that carbene complexes of group 10 metals have been successfully applied in chain growth reactions. In 1999 Herrmann and co-workers reported for the first time the copolymerization of CO−ethylene using dicationic chelating carbene complexes of Pd^{II}.[5] It was concluded that the percentage of precatalyst that is actually participating in the polymerization reaction would appear to be small. This conclusion combined with the modest turnover numbers observed for these catalyst systems prompted us to investigate the carbonylation chemistry of a Me−Pd carbene complex. We report here studies that demonstrate the occurrence of migratory insertion of CO into the Pd−Me bond of heterocyclic carbene complexes, which is then followed by rapid decomposition via elimination of acylimidazolium salts.



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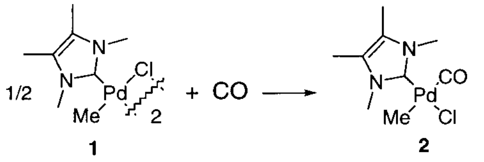
Results and Discussion

A $Me{-}Pd^{II}$ carbene complex with ligated CO (**2**) is conveniently prepared by a bridge-splitting reaction of the dimer $[PdMe(tmiy)Cl]_2$ (**1**)[9,15] (tmiy = 1,3,4,5-tetramethylimidazolin-2-ylidene) with CO at −40 °C (reaction 2). In the ^1H NMR spectrum (−40 °C) of **2** signals for the NCH_3 and CCH_3 protons occur as two singlets at 3.73 and 2.11 ppm, respectively, compared with four



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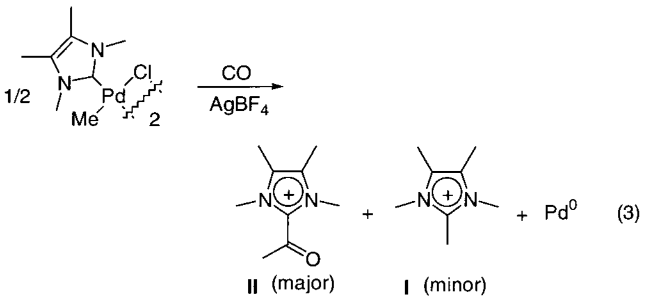
singlets at 3.91, 3.87, 2.10, and 2.08 ppm for the two isomers of **1** present at this temperature. The $PdCH_3$ signal occurs at 0.50 ppm, downfield from those at 0.27 and 0.23 ppm in the precursor **1**. Coordination of CO is further verified by a strong peak at 2112 cm^{-1} in the IR spectrum of the complex.[16] Migratory insertion of CO into the Pd−Me bond of **2** was not directly observed during variable-temperature NMR experiments; however the complex is thermally unstable and decomposes at room temperature to give 1,2,3,4,5-pentamethylimidazolium chloride (**I**) as the major product by NMR along with Pd^0. Thus, reductive carbene−methyl coupling and elimination appear to be more facile than CO insertion into the Pd−Me bond for complex **2**. However, the preferred formation of pentamethylimidazolium may be a result of the structure of **2**; see later discussion. In the mass spectrum (LSIMS, liquid secondary ion mass spectroscopy) of a solution of decomposed **2** the major peak corresponds to the pentamethylimidazolium ion ($m/z = 139$); however a small peak of 5% abundance ($m/z = 167$) is also observed, which is consistent with the 2-acyl-1,3,4,5-tetramethylimidazolium cation (**II**). It is evident therefore, that some insertion of CO into the Pd−Me bond has occurred to give an acyl Pd intermediate, which then decomposes via elimination of an acylimidazolium salt.

When **1** is treated with $AgBF_4$ in the presence of CO, decomposition is very rapid and Pd^0 deposits even at −20 °C. After decompositon the major product in this case is the acylimidazolium ion **II** with a small amount (ca. 15% by NMR) of the pentamethylimidazolium ion **I** (reaction 3). The mass spectrum (LSIMS) of the decomposition residue shows the acylimidazolium ion as the major signal along with a smaller peak for the pentamethylimidazolium ion. The 2-acyl-1,3,4,5-tetramethylimidazolium tetrafluoroborate obtained by recrystallization of the residue has been characterized by ^1H and ^{13}C NMR, IR spectroscopy, and CHN analysis.



In an attempt to identify an acyl−Pd intermediate low-temperature NMR spectroscopy was performed. Complex **2** was treated with a slight excess of $AgBF_4$ at −50 °C, and changes in the ^1H NMR spectrum were recorded as the temperature was raised. No reaction is observed until −20 °C, whereupon the signals due to **2** are replaced with broad resonances at 4.09 and 2.13 ppm for the carbene moiety. The Pd−Me signal disappears and a signal at 2.33 ppm grows in its place. At this temperature the signals were too broad to obtain a ^{13}C NMR spectrum, while at room temperature the signals sharpen but decomposition is more rapid. Thus we were unable to satisfactorily characterize the intermediate, but the methyl peak at 2.33 ppm is consistent with a Pd−acyl species.[17−20] When the reaction was carried out at −20 °C in DCM and the solution analyzed by IR spectroscopy, a carbonyl peak at 1711 cm^{-1} was observed. This once again is consistent with a Pd−acyl species.[17−20] Upon complete decomposition, the acylimidazolium shows a carbonyl peak at 1699 cm^{-1}.

The above results may be rationalized in terms of the need for CO to be cis to the methyl group in order for migratory insertion of CO to occur. In complex **2** the CO ligand is most likely trans to the methyl group,[21] thus requiring a preinsertion isomerization[22] before migratory insertion can proceed. When the halide ligand is abstracted, the position cis to the methyl group is no longer blocked, and hence CO insertion does not require a prior isomerization step and may compete effectively with the methyl−carbene elimination reaction.

Most importantly, these observations show that acyl−Pd complexes are prone to the same mode of decomposition as hydrocarbyl−Pd and −Ni carbene complexes and that this reaction can be a very facile process. In both of the above examples CO insertion does occur, but is accompanied by elimination of acyl imidazolium salts, leading to decomposition. The fact that in each case both the acyl and methyl imidazolium ions are formed indicates that CO insertion and carbene−hydrocarbyl elimination occur at comparable rates in the present system. Thus, this reaction represents a likely route to catalyst deactivation for CO/ethylene copolymerization catalysts based on Pd or Ni carbenes, in which the growing polymer chain would be bound to the metal through alternating alkyl and acyl bonds. We are currently completing combined theoretical and kinetic studies in an attempt to deduce the detailed mechanism of this decomposition reaction.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques or in a nitrogen glovebox. All solvents were purified by standard procedures and distilled under nitrogen immediately prior to use. NMR spectra were recorded on a Varian Gemini-200 NMR spectrometer at 199.98 MHz (^1H) and 50.289 MHz (^{13}C), and chemical shifts (δ) are reported in units of ppm relative to internal TMS. Elemental analysis and MS were carried out by the Central Science Laboratory, University of Tasmania, on a Carlo Erba EA1108 elemental analyzer and a Kratos Concept ISQ MS, respectively. Characterization of the pentamethylimidazolium ion has previously been reported.[9,10]

PdMeCl(tmiy)CO (2). An NMR sample of $[PdMe(tmiy)Cl]_2$ (**1**)[9,15] at −40 °C was treated with CO for several minutes,

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causing the signals to shift due to the quantitative formation of PdMeCl(tmiy)CO (**2**). δ_H (200 MHz, CD_2Cl_2, −40 °C): 3.73 (s, 6H, NCH_3), 2.11 (s, 6H, CCH_3), 0.50 (s, 3H, $PdCH_3$). δ_C (50 MHz, CD_2Cl_2, −40 °C): 181.9 ($C{=}O$), 171.9 (NCN), 126.3 ($HC{=}CH$), 36.2 (NCH_3), 9.9 (CCH_3), −11.4 ($PdCH_3$). LSIMS *m*/*z*: 139 [1,2,3,4,5-pentamethylimidazolium]$^+$. Addition of ether afforded a white precipitate that was dried in vacuo at −30 °C. Anal. Found: C, 34.58; H, 4.75. $C_9H_{15}N_2OClPd$ requires: C, 34.97; H, 4.89. IR (DCM): 2112 cm^{-1}.

2-Acyl-1,3,4,5-tetramethylimidazolium (II). The procedure for the preparation of **1** was repeated with the addition of 1 equiv of $AgBF_4$, leading to decomposition and formation of Pd deposits. LSIMS of the solution: *m*/*z* 167.1 [2-acyl-1,3,4,5-tetramethylimidazolium]$^+$ (100%); 139 [1,2,3,4,5-pentamethylimidazolium]$^+$ (35%). Filtration through Celite and repeated recrystallization from DCM/ether gave pure 2-acyl-1,3,4,5-tetramethylimidazolium tetrafluoroborate. Anal. Found: C, 42.44; H, 5.66; N, 11.43. $C_9H_{15}N_2OBF_4$ requires C, 42.55; H, 5.95; N, 11.03. δ_H (200 MHz, $CDCl_3$): 3.87 (s, 6H, NCH_3), 2.78 (s, 3H, $C(O)CH_3$), 2.31 (s, 6H, CCH_3). δ_C (50 MHz, $CDCl_3$): 188.4 ($C{=}O$), 185.7 (NCN), 129.8 ($C{=}C$), 34.4 (NCH_3), 31.0 ($C(O)CH_3$), 9.0 (CCH_3). IR (DCM): 1699 cm^{-1}.

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