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Acyl−Carbene and Methyl−Carbene Coupling via Migratory Insertion in Palladium Complexes

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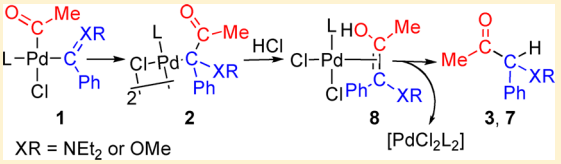
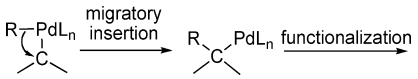
ABSTRACT: The migratory insertion reaction of a carbene into a palladium−acyl bond has been observed both for monoaminocarbenes and for methoxycarbenes. The acyl derivative [PdCl(COMe){C(NEt$_2$)-Ph}(PPh$_3$)] undergoes an acyl−carbene coupling, leading to the enolate-type complex [PdCl{C(COMe)(NEt$_2$)Ph}(PPh$_3$)]$_2$ (**2**). This complex decomposes either by reductive elimination to give the iminium salt or by protonation of the enolate to give a ketoamine. In a similar fashion, the reaction of [Pd$_2$(μ-Cl)$_2$(COMe)$_2$(SMe$_2$)$_2$] with [W(CO)$_5${C(OMe)Ph}] leads to an undetected palladium enolate that, after protonation, is stabilized by coordination to palladium ([PdCl$_2${(OH)MeC═CPh(OMe}(SMe$_2$)], **8**). The reaction of [Pd$_2$(μ-Cl)$_2$Me$_2$(SMe$_2$)$_2$] with [W(CO)$_5${C(OMe)-Ph}] leads to the migratory insertion of the carbene into the Pd−methyl group to give an alkyl palladium complex. The transfer of CO from tungsten, followed by insertion into the Pd−Me group, also occurs. This leads to the formation of a Pd−COMe group, which also undergoes migratory insertion of the carbene fragment. These results support that migratory insertion is a key C−C coupling step, as proposed for the new Pd-catalyzed transformations that use carbene precursors.



INTRODUCTION

New Pd-catalyzed transformations that use carbene precursor reagents, such as diazoalkanes,[1,2] tosylhydrazones,[2,3] or group 6 metal carbenes,[4] have been devised recently. In these reactions, a migratory insertion in putative palladium carbene intermediates is deemed responsible for the key C−C coupling step, which leads to a new alkyl group on palladium, susceptible of further functionalization (Scheme 1). As a result, the reactions are highly efficient transformations often introducing at least two different functional groups or building several C−C bonds in one process.

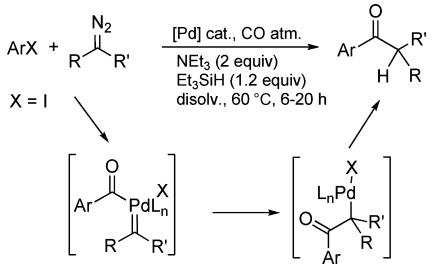
Scheme 1. Key C−C Coupling Step for Pd-Catalyzed Reactions That Use Carbene Precursors



Just a few years back, migratory insertion was unknown for palladium carbene complexes [PdR(carbene)L$_2$], but we proved that this transformation did occur for R = pentafluorophenyl.[5] Another example was reported later by Danopoulos et al., who synthesized a Pd complex containing a chelating carbene−alkyl ligand and proposed that the alkyl fragment had resulted from migratory insertion of an N-heterocyclic carbene ligand into a Pd−Me bond.[6]

Among the new tandem transformations that use carbene precursors and are believed to involve a migratory insertion step, Wang et al. reported an interesting Pd-catalyzed synthesis of keto derivatives from aryl iodides, CO, and diazoalkanes as carbene precursors (Scheme 2).[2] They proposed that a carbonylation by CO and a migratory insertion of carbene into the Pd−acyl bond took place (Scheme 2). The migratory insertion of carbene ligands into metal−acyl bonds is not frequent, and only a few stoichiometric examples have been reported for Mo and W complexes.[7] In addition, this reaction has been proposed to occur in the formation of cyclic ketones from alkoxycarbene complexes of chromium,[8] and the formation of acylimidazolium salts from *N*,*N*-heterocyclic palladium carbenes involves an acyl−carbene coupling.[9]

Scheme 2. Proposed Mechanism for the Multicomponent Pd-Catalyzed Synthesis of Keto Derivatives



We have been interested in learning about this reaction by checking in a more direct way whether, as proposed in the many references above, carbenes do insert in Pd−acyl bonds and can insert into other Pd−R bonds. We show here that alkoxo- or aminocarbenes on Pd−acyl complexes indeed undergo migratory insertion reactions. Moreover, the characterization of the key intermediates in this process support that carbenes also insert in Pd−alkyl bonds.

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RESULTS

Our observations come from the study of the decomposition of acyl−palladium amino- or methoxycarbenes. The experimental protocol for these studies was the following: $CDCl_3$ solutions of a preformed acyl palladium aminocarbene or in situ generated acyl palladium methoxycarbenes were monitored by NMR; intermediate organometallic complexes and organic products were spectroscopically characterized using multinuclear NMR and $^1H-^{13}C$ NMR HMBC experiments. The results of these experiments are described in detail below. Isolation of the products was attempted by repeating the reactions in Schlenk tubes, adjusting the reaction time to maximize the concentration of the target species. Since mixtures of products were produced in all cases, partial separation by chromatography was carried out. In this way, the characterization of the involved species was completed, but we failed to isolate pure species or to obtain X-ray quality crystals for structure determination.

The complex *trans*-[PdCl(COMe){C(NEt$_2$)Ph}(PPh$_3$)] (*trans*-**1**; *trans* refers to the relative phosphine−carbene arrangement) was synthesized by reaction of [Pd$_2$(μ-Cl)$_2$Me$_2$(SMe$_2$)$_2$] with [W(CO)$_5${C(NEt$_2$)Ph}], followed by addition of PPh$_3$, as reported before.[10] This reaction involves the transfer of carbene and CO from W to Pd, which leads to the formation of the acyl group bound to palladium. *trans*-**1** undergoes isomerization in solution ($CDCl_3$) at room temperature (Figure 1) to *cis*-**1** ($^2J_{C,P}$ = 5.0 Hz for the carbene carbon

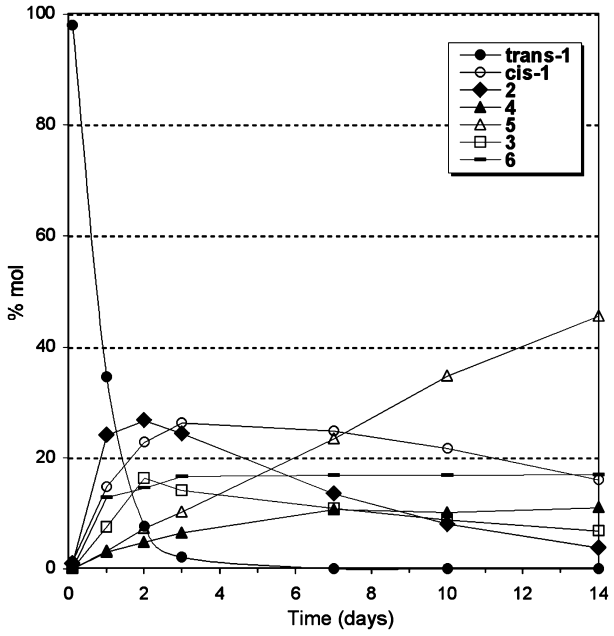
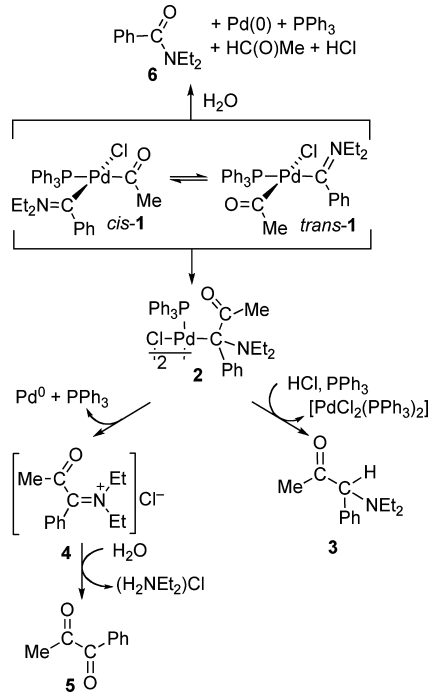


Figure 1. Kinetic profile for the evolution of complex *trans*-**1** in $CDCl_3$ solution (% of the carbene decomposition products vs time).

resonance in ^{13}C NMR vs $^2J_{C,P}$ = 102.1 Hz for *trans*-**1**). Both isomers bear the acyl group cis to the carbene ligand, and both undergo migratory insertion to give **2** (Scheme 3).[11]

The decomposition of *cis*-**1** is slower, and this complex stays in solution for weeks, eventually decomposing to the same products as *trans*-**1**. Complexes **1** also decompose at the beginning of the reaction by direct hydrolysis of the carbene moiety with adventitious water,[12] to give diethylbenzamide (**6**) and acetaldehyde.[13] A kinetic profile of the whole process monitored in an NMR tube is given in Figure 1. The

Scheme 3. Decomposition Pathways of Complexes 1



disappearance of *trans*-**1**, as measured by initial rates, is first order in the palladium complex and is independent of the concentration of PPh$_3$.

Complex **2** is an enolate derivative that shows a Pd-C ^{13}C NMR resonance at 111 ppm and $^2J_{C,P}$ = 5.0 Hz, consistent with a cis alkyl−phosphine arrangement. The ^1H NMR pattern for the amino group shows chemical equivalence for the ethyl groups (by fast rotation about the (Pd)C−N bond and inversion of the lone pair on N), but diastereotopic methylene protons (Figure 2). This is consistent with the structure

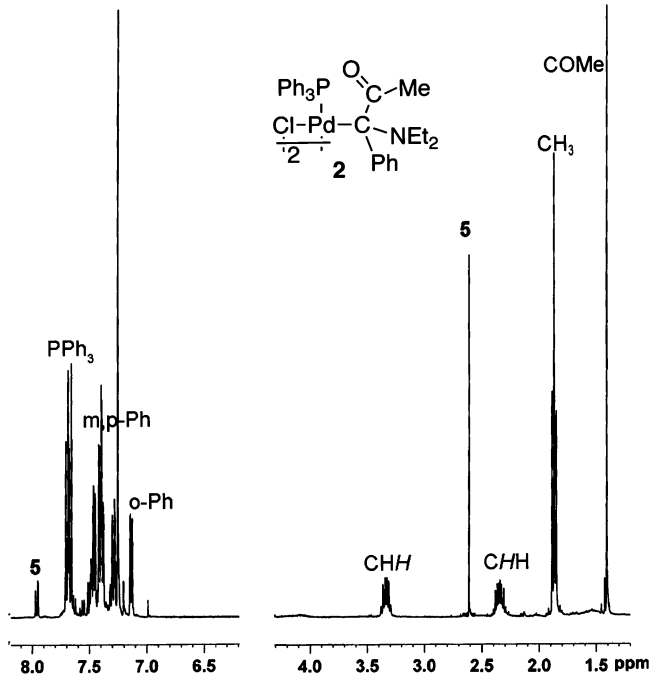


Figure 2. ^1H NMR spectrum of **2** (a small amount of **5** is present).

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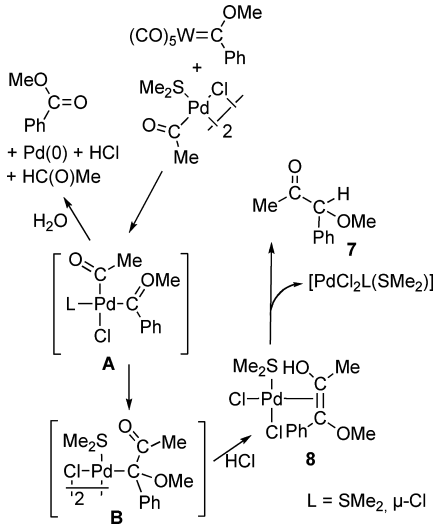
depicted for **2**. Complex **2** undergoes two types of reactions: (i) protonation to give the ketoamino derivative **3** and (ii) reductive elimination to give the iminium salt **4**, and subsequent hydrolysis to the diketone **5**. Protonation of palladium enolate complexes is a very facile process,[14] and the acid generated in the formation of **6** or **5** can easily produce **3**. The iminium derivative **4** was clearly identified by the characteristic C═N ^{13}C NMR signal at 170 ppm, as well as the MeCO resonance at 201.2 ppm. As expected, two non-equivalent ethyl substituents on the nitrogen are observed for **4** in the ^{1}H and ^{13}C NMR spectra (see the Experimental Section).

In a similar study, the transmetalation of the analogous methoxycarbene moiety from W to Pd, does not allow the detection of the corresponding acyl palladium methoxycarbenes **A**, because a subsequent fast migratory insertion reaction occurs (Scheme 4). Thus, the reaction of $[W(CO)_5\{C(OMe)Ph\}]$

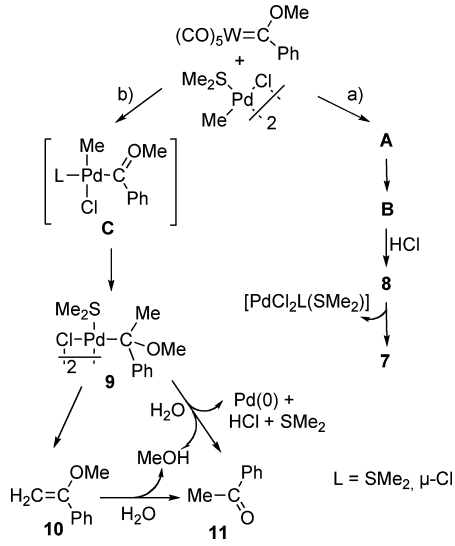
Scheme 4. Migratory Insertion Reaction of a Methoxycarbene into a Pd−Acyl Bond



and the acyl palladium complex $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(SMe_2)_2]$ in CD_3CN leads to the methoxyketone **7** (Scheme 4). The formation of **7** must proceed via transmetalation to give the palladium methoxycarbene (**A**), followed by migratory insertion into the Pd−acyl moiety to give the enolato complex **B**, in the same way it was described above for **1**. Protonation of **B** leads to **8**, which finally releases **7**. Complex **8** was detected when the reaction was monitored by ^{1}H NMR and was characterized with the aid of ^{1}H−^{13}C NMR HMQC and HMBC experiments. Complex **8** shows a hydroxoalkene ligand, the enol tautomer of **7**, coordinated to palladium. It is a mixture of two isomers ($\mathbf{8}_1$, major, and $\mathbf{8}_2$, minor), which we assign to the *E* and *Z* isomers of the coordinated hydroxoalkene. Each isomer shows characteristic signals at δ 5.71 ($\mathbf{8}_1$) and 6.28 ($\mathbf{8}_2$), which are assigned to the hydroxy resonances. A ^{1}H−^{13}C NMR HMBC experiment at low temperature shows long-range coupling of the ^{1}H O*H* and ═C-*Me* resonances to both olefinic carbons at 143.5, 134.0 ppm ($\mathbf{8}_1$) and 139.2, 133.2 ppm ($\mathbf{8}_2$). The reaction in Scheme 4 is faster than that for **1** (it is complete in 9 h, compared with days for **1**). As was the case for the amino derivatives, the direct products of hydrolysis of the palladium methoxycarbene (methyl benzoate and Pd(0)) were also observed.

Finally, the reaction of $[W(CO)_5\{C(OMe)Ph\}]$ and the methyl palladium complex $[Pd_2(\mu\text{-}Cl)_2Me_2(SMe_2)_2]$ shows reaction intermediates and products formed by migratory insertion into both a Pd−Me and a Pd−acyl bond (Scheme 5).

Scheme 5. Migratory Insertion Reactions of a Methoxycarbene into a Pd−Acyl and a Pd−Me Bond



The latter results from carbene plus CO transfer from tungsten to palladium and CO insertion into the Pd−Me bond (path a, Scheme 5). The reactivity is the same as that observed for the acyl precursor in Scheme 4. This is the preferred pathway, and **7** accounts for 60% of the decomposition products. Although the palladium carbene complex **C** could not be observed, it must be formed, and the coupling of methyl and carbene also occurs since the product of migratory insertion **9** could be detected in solution (^{13}C NMR Pd-*C*, 101.7 ppm). This complex decomposes by β-H elimination to the enol ether **10**, and eventually by hydrolysis of **9** and **10** to the ketone **11**. Table 1 shows the percentages of the decomposition products after 30 min and the final distribution.

Table 1. Product Distribution (%) for the Reaction in Scheme 5

compound or pathway	30 min	9 h
$[Pd_2(\mu\text{-}Cl)_2Me_2(SMe_2)_2]$	21.4	
pathway a	38.8 (**7**, 3.5; **8**, 35.2)	59.7 (**7**)
pathway b	35.4 (**9**, 9.9; **10**, 13.4; **11**, 12.1)	35.4 (**11**)
hydrolysis[a]	4.4 (PhC(O)Me)	4.9 (PhC(O)Me)

[a]Hydrolysis of the carbene fragment in **A** or **C**.

DISCUSSION

The results obtained clearly show that both amino- and methoxycarbenes insert into Pd−acyl bonds to give keto derivatives as final products. All the steps in this transformation have been proved by characterization of the intermediates involved, as shown in the discussion. These results strongly support Wang's mechanistic proposal for the multicomponent coupling of diazo derivatives and arylhalides in the presence of CO (Scheme 2).[2]

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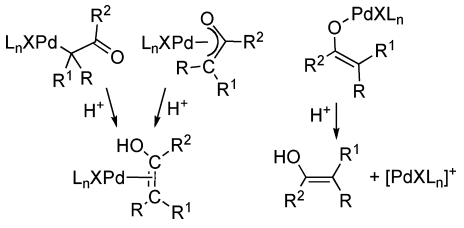
The reported examples of coupling of R groups on palladium complexes with monoamino-[5] or diaminocarbenes[15] usually leads to iminium salts as final products. This reaction is indistinguishable from a reductive elimination. The characterization of **2** shows that, at least for monoaminocarbenes, the coupling is a migratory insertion reaction, followed, when iminium salts are formed, by a reductive decomposition. The R−carbene coupling occurs by the same process for monoamino- or alkoxocarbenes, although at a much faster rate for the more electrophilic methoxycarbenes. This prevents the detection of the intermediate methoxycarbene palladium complexes that should form by transmetalation, whereas they have been characterized when no migratory insertion can follow.[13] Although the different nature of the L ligand coordinated to palladium could have some influence on the rate of migratory insertion (L = PPh_3 for **1** or L = μ-Cl, SMe_2 for **A** or **C**), this difference is small compared to the change in nature of the carbene ligand, as shown in our former work with R = C_6F_5,[5b,c] and as suggested by the fact that none of the methoxycarbene complexes could be detected.

A β-H elimination process, frequent for many palladium alkyls, is not possible for **2**. On the other hand, this alkyl group is an enolate-type ligand that, as expected, undergoes electrophilic attack by H^+ to the oxygen atom, which is the more nucleophilic center. Palladium enolates can show different coordination modes, such as C-bonded,[14,16,17] O-bonded,[17,18] and η^3-oxoallyl-type.[19] Most of them are C-bonded, and this is the case of **2**. However, an equilibrium with molecules showing the other bonding types, transient or in undetectable concentration, could be responsible for the reactivity observed. Complex **8** is the result of protonation and shows that the enol form is strongly stabilized by coordination. We believe that the characterization of **8** indicates that the protonation of **2** via an O-bonded enolate intermediate is the least plausible route in this case, since a fast decoordination should be expected in the presence of other competing ligands, such as SMe_2, or acetonitrile as solvent. On the other hand, if protonation occurs on the carbonyl group of the C-bonded palladium enolate or, better, on the more basic oxygen of an η^3-oxoallyl, the resulting vinyl alcohol product is already coordinated to the metal (Scheme 6). Although the η^3-oxoallyl form is not a coordination mode commonly observed for palladium, it should be carefully considered to explain enolate reactivity.

Scheme 6. Protonation of Different Isomeric Forms of Palladium Enolates



CONCLUSION

The migratory insertion reaction of both methoxy- and monoaminocarbenes into a Pd−acyl group has been observed. The characterization of relevant intermediates **2** and **8** clearly shows the main steps of the decomposition pathway. The migratory insertion reaction of a methoxycarbene into a Pd−Me bond has also been supported by the characterization of complex **9**. These findings show that the migratory insertion in palladium carbenes is fairly general and includes Pd−Ar (Ar = C_6F_5),[5] Pd−acyl, and Pd−alkyl bonds. This means that it is certainly a most plausible fundamental step in palladium-catalyzed transformations whenever palladium carbene intermediates can be formed.

EXPERIMENTAL SECTION

General Methods. ^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC-300, ARX-300, and AV-400 spectrometers. Chemical shifts (in δ units, parts per million) were referenced to Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). The spectral data were recorded at 293 K unless otherwise noted. GC-mass spectra were recorded on a Thermo Scientific Focus DSQII system.

All the manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents under nitrogen, prior to use. Complexes $[Pd(\mu\text{-Cl})Me(SMe_2)]_2$,[20] $[Pd(\mu\text{-Cl})COMe(SMe_2)]_2$,[10,21] *trans*-[PdCl(COMe){C(NEt$_2$)Ph}(PPh$_3$)] (**1**),[10] and $[W(CO)_5\{C(OMe)Ph\}]$[22] were prepared according to literature methods. Compounds **5**, **6**, **10**, **11**, and Ph(CO)OMe are known and commercial. They were completely characterized in the reaction mixtures or compared with authentic samples, but their spectroscopic data are not included here.

Decomposition of trans-[PdCl(COMe){C(NEt$_2$)Ph}(PPh$_3$)] (trans-1). A solution of *trans*-**1** (0.008, 0.008 mmol) in $CDCl_3$ (0.6 mL) was prepared in a 5 mm NMR tube under nitrogen at room temperature. The solution was monitored by ^1H and $^{31}P\{^1H\}$NMR spectroscopy over a period of days. The decomposition products were characterized in the mixture, and percentages of products are shown in Figure 1.

The reaction was repeated using 50 mg of *trans*-**1**. Partial separation of the products was carried out as follows: *cis*-**1** was obtained by precipitation in Et_2O of the mixture kept at room temperature for 3 days; **2** and **3** were separated from the mother liquors by preparative TLC using Et_2O as eluent.

cis-**1**: ^1H NMR (400 MHz, δ, $CDCl_3$): 7.50−7.28 (m, 18H; PPh_3), 7.19 (m, 3H; H_{meta} Ph, H_{para} Ph), 6.67 (m, 2H; H_{ortho} Ph), 5.31 (m, 1H; C*H*H), 4.39 (m, 1H; C*H*H), 3.46 (m, 2H; CH′$_2$), 1.97 (s, 3H; C(O)*Me*), 1.70 (t, J = 7.2 Hz, 3H; C*H*$_3$), 1.01 (t, J = 7.2 Hz, 3H; CH′$_3$). ^1H NMR (400 MHz, δ, $CDCl_3$, 243 K): 7.50−7.28 (m, 18H; PPh_3), 7.20 (m, 3H; H_{meta} Ph, H_{para} Ph), 6.58 (br, 2H; H_{ortho} Ph), 5.40 (m, 1H; C*H*H), 4.33 (m, 1H; C*H*H), 3.46 (m, 2H; CH′$_2$), 1,90 (s, 3H; C(O)*Me*), 1.71 (t, J = 7.2 Hz, 3H; CH_3), 1.02 (t, J = 7.2 Hz, 3H; CH′$_3$). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 25.33 (s). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$, 243 K): 25.42 (s). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 230.4 (d, $^2J_{C,P}$ = 5.0 Hz, Pd-$C_{carbene}$), 221.7 (s, *C*(O)Me), 139.2 (s, C_{ipso} Ph), 134.4 (d, $^2J_{C,P}$ = 12.1 Hz, C_{ortho} PPh_3), 131.1 (s, C_{para} PPh_3), 130.5−128.0 (12C, C_{ipso} PPh_3, C_{meta} PPh_3, C_{meta} Ph, C_{para} Ph), 125.1 (s, C_{ortho} Ph), 57.3 (s, CH_2), 47.4 (s, C′H_2), 36.7 (d, $^3J_{C,P}$ = 28.2 Hz, C(O)*Me*), 13.0 (s, CH_3), 11.9 (s, C′H_3).

2: ^1H NMR (400 MHz, δ, $CDCl_3$): 7.68 (m, 6H; H_{ortho} PPh_3), 7.43 (m, 3H; H_{para} PPh_3), 7.39 (m, 6H; H_{meta} PPh_3), 7.29 (m, 3H; H_{meta} Ph, H_{para} Ph), 7.14 (m, 2H; H_{ortho} Ph), 3.35 (m, 2H, C*H*H, CH_2), 2.35 (m, 2H, CH*H*, CH_2), 1.88 (t, J = 7.2 Hz, 6H; CH_3), 1.42 (s, 3H; C(O)*Me*). ^1H NMR (400 MHz, δ, $CDCl_3$, 243 K): 7.65 (m, 6H; H_{ortho} PPh_3), 7.50 (m, 3H; H_{para} PPh_3), 7.43 (m, 6H; H_{meta} PPh_3), 7.30 (m, 3H; H_{meta} Ph, H_{para} Ph), 7.13 (m, 2H; H_{ortho} Ph), 3.31 (m, 2H, C*H*H, CH_2), 2.34 (m, 2H, CH*H*, CH_2), 1.89 (t, J = 7.2 Hz, 6H; CH_3), 1.42 (s, 3H; C(O)*Me*). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 23.54 (s). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$, 243 K): 23.82 (s). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, $CDCl_3$, 243K): 164.8 (d, $^3J_{C,P}$ = 3.02 Hz, *C*(O)Me), 134.7 (d, $^2J_{C,P}$ = 11.1 Hz, 2C; C_{ortho} PPh_3), 133.7 (s, C_{ipso} Ph), 132.7 (s, 2C; C_{ortho} Ph), 131.0 (s, C_{para} PPh_3), 128.5 (d, $^1J_{C,P}$ = 53.3 Hz, C_{ipso} PPh_3), 128.3 (d, $^3J_{C,P}$ = 11.1 Hz, 2C; C_{meta} PPh_3), 127.5 (s, 2C; C_{meta} Ph), 111.0 (d, $^2J_{C,P}$ = 5.0 Hz; Pd-*C*), 52.4 (d, $^4J_{C,P}$ = 2.0 Hz, 2C; $2CH_2$), 19.1 (s, C(O)*Me*), 13.5 (s, 2C; $2CH_3$).

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3: ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.50−7.25 (5H; Ph)*, 4.31 (s, 1H; C*H*), 2.65 (m, 2H; C*H*H, $2CH_2$), 2.48 (m, 2H; CH*H*, $2CH_2$), 2.14 (s, 3H; C(O)*Me*), 0.99 (t, J = 7.2 Hz, 6H; $2CH_3$). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, $CDCl_3$, 243K): 209.2 (s, *C*(O)Me), 135.4 (s, C_{ipso} Ph), 129.2 (s, C_{orto} Ph), 128.8 (s, C_{para} Ph), 128.3 (s, C_{meta} Ph)*, 77.2 (s, *C*-H), 42.4 (s, 2C; $2CH_2$), 26.4 (s, C(O)*Me*), 10.1 (s, 2C; $2CH_3$). MS (EI) m/z (%): 205 (1) $[M]^+$, 162 (100), 134 (12), 77 (10) (* = signals overlap with signals of other compounds).

4: ^{1}H NMR (400 MHz, δ, $CDCl_3$, 243 K): 8.00 (m, 2H; H_{ortho} Ph), 7.80−7.30 (m, 3H; H_{meta}, H_{para} Ph), 3.35 (q, J = 7.2 Hz, 2H; CH_2), 3.28 (q, J = 7.2 Hz, 2H; CH'_2), 2.09 (s, 3H; C(O)*Me*), 1.16 (t, J = 7.2 Hz, 3H; CH_3), 1.10 (t, J = 7.2 Hz, 3H; CH'_3). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 201.2 (s, *C*(O)Me), 170.0 (s, *C*=N), 136.9 (s, C_{para} Ph), 133.6 (s, C_{ipso} Ph), 130.4 (s, C_{ortho} Ph), 130.0 (s, C_{meta} Ph), 42.8 (s, CH_2), 39.9 (s, $C'H_2$), 21.8 (s, C(O)*Me*), 14.1 (s, CH_3), 13.1 (s, $C'H_3$).

Reaction of [W(CO)$_5${C(OMe)Ph}] and [Pd(μ-Cl)(Me)(SMe$_2$)]$_2$. $[Pd(\mu\text{-Cl})(Me)(SMe_2)]_2$ (0.0150 g, 0.0337 mmol) was added to a solution of $[W(CO)_5\{C(OMe)Ph\}]$ (0.0300 g, 0.0675 mmol) in CD_3CN (0.6 mL). The solution was then examined by ^{1}H NMR spectroscopy, and the resulting products were identified. Product ratios are given in the text. The separation of the products was carried out by preparative TLC using Et_2O as eluent.

The reaction of $[W(CO)_5\{C(OMe)Ph\}]$ and $[Pd(\mu\text{-Cl})(COMe)(SMe_2)]_2$ was carried out in the same way.

7: ^{1}H NMR (400 MHz, δ, CD_3CN): 7.38 (m, 5H; Ph), 4.71 (s, 1H; C*H*), 3.33 (s, 3H; OMe), 2.07 (s, 3H; C(O)*Me*). ^{1}H NMR (400 MHz, δ, CD_3CN, 243 K): 7.38 (m, 5H; Ph), 4.74 (s, 1H; C*H*), 3.26 (s, 3H; OMe), 2.04 (s, 3H; C(O)*Me*). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, CD_3CN): 207.6 (s, *C*(O)Me), 137.7 (s, 2C; C_{ipso} Ph), 129.7 (s, 2C; C_{meta} Ph), 129.4 (s, 2C; C_{para} Ph), 128.2 (s, 2C; C_{ortho} Ph), 89.9 (s, *C*H), 57.6 (s, O*Me*), 25.8 (s, C(O)*Me*). MS (EI) m/z (%): 164 (1) $[M]^+$, 121 (100), 105 (18), 91 (42), 77 (86), 63 (5), 51 (14), 43 (11).

8: This complex is a mixture of two isomers, $\mathbf{8_1}$ and $\mathbf{8_2}$ (see text).

$\mathbf{8_1}$: ^{1}H NMR (400 MHz, δ, CD_3CN): 7.63 (m, 2H; H_{ortho} Ph), 7.33 (m, 2H; H_{meta} Ph), 7.17 (m, 1H; H_{para} Ph), 5.71 (s, OH), 3.39 (s, 3H; OMe), 2.27 (s, 6H; SMe_2), 2.05 (s, 3H; =C-*Me*). ^{1}H NMR (400 MHz, δ, CD_3CN, 243 K): 7.63 (m, 2H; H_{ortho} Ph), 7.33 (m, 2H; H_{meta} Ph), 7.16 (m, 1H; H_{para} Ph), 6.15 (s, OH), 3.36 (s, 3H; OMe), 2.21 (s, 6H; SMe_2), 2.03 (s, 3H; =C-*Me*). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, CD_3CN, 243 K): 143.5 (s, (OH)Me-*C*=), 134.9 (s, C_{ipso} Ph), 134.0 (s, =*C*-OMe(Ph)), 128.5 (s, 2C; C_{ortho} Ph), 126.6 (s, 2C; C_{meta} Ph), 126.1 (s, C_{para} Ph), 58.9 (s, O*Me*), 21.3 (s, 2C; SMe_2), 16.2 (s, =C-*Me*).

$\mathbf{8_2}$: ^{1}H NMR (400 MHz, δ, CD_3CN): 7.80−7.25 (m, 4H; H_{ortho}, H_{meta} Ph), 7.17 (m, 1H; H_{para} Ph), 6.28 (s, OH), 3.35 (s, 3H; OMe), 2.21 (s, 6H; SMe_2), 1.84 (s, 3H; =C-*Me*). ^{1}H NMR (400 MHz, δ, CD_3CN, 243 K): 7.80−7.25 (m, 4H; H_{ortho}, H_{meta} Ph), 7.22 (m, 1H; H_{para} Ph), 6.53 (s, OH), 3.30 (s, 3H; OMe), 2.27 (s, 6H; SMe_2), 1.83 (s, 3H; =C-*Me*). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, CD_3CN, 243 K): 139.2 (s, (OH)Me-*C*=), 134.2 (s, C_{ipso} Ph), 133.2 (s, =*C*-Ph(OMe)), 130.0−125.0 (5C; C_{ortho}, C_{meta}, C_{para} Ph), 57.7 (s, O*Me*), 21.3 (s, 2C; SMe_2), 15.4 (s, =C-*Me*).

9: ^{1}H NMR (400 MHz, δ, CD_3CN): 7.65* (m, 2H; H_{ortho} Ph), 7.47* (m, 3H; H_{meta}, H_{para} Ph), 3.13 (s, 3H; OMe), 2.21 (s, 6H; SMe_2), 1.48 (s, 3H; Me). ^{1}H NMR (400 MHz, δ, CD_3CN, 243 K): 7.50−7.40 (m, 3H; H_{meta}, H_{para} Ph), 7.40−7.30 (m, 2H; H_{ortho} Ph), 3.09 (s, 3H; OMe), 2.27 (s, 6H; SMe_2), 1.45 (s, 3H; Me). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, CD_3CN, 243 K): 143.4 (s, C_{ipso} Ph), 129.4 (s, 2C; C_{ortho} Ph), 127.4 (s, 2C; C_{meta} Ph), 126.5 (s, C_{para} Ph), 101.7 (s, Pd-*C*), 48.6 (s, O*Me*), 26.0 (s, Me), 21.3 (s, 2C; SMe_2) (* = signal overlaps with signals of other compounds).

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Notes

The authors declare no competing financial interest.

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(11) We are drawing in all the schemes the resonant form that better represents the bonding in monoamino or monoalkoxo Pd−carbenes. The molecular structures of palladium monoaminocarbenes show short C−X bond lengths and Pd−C bond distances fully consistent with a single bond (see, for example, refs 5b−d and 10). The reactivity of palladium alkoxocarbenes characterized in solution also indicates the strong contribution of the depicted resonant form (see ref 13).

(12) Note that the importance of this hydrolysis is exaggerated in Figure 1 because the amount of reagent in the NMR tube is very small.

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