Carbene and Carbonyl Transfer from [W(CO)$_5$(carbene)] to Palladium, Affording Palladium(II) Carbene Acyl Complexes

Isabel Meana, Ana C. Albéniz,* and Pablo Espinet*

IU CINQUIMA/Química Inorgánica, Universidad de Valladolid, 47071-Valladolid, Spain

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The reaction of [W(CO)$_5${C(NEt$_2$)Ph}] (**3**) with [PdClR(SMe$_2$)]$_2$ (R = Me, Ph) occurs with transfer of carbene and carbonyl groups to give [PdCl{C(O)R}{C(NEt$_2$)Ph}]$_2$ (R = Me, **4**; R = Ph, **5**). When the reaction is monitored for R = Me, only [PdCl(COMe)(SMe$_2$)]$_2$ and the final carbene **4** are observed, suggesting that the transfer and insertion of the carbonyl group are faster than the carbene transmetalation. Although CO insertion into M−X bonds is thermodynamically excluded in many systems (e.g., in M−halogen and M−C$_6$F$_5$ bonds), this study warns of the fact that CO is easily available when [M(CO)$_5$(carbene)] complexes are used as carbene sources, whether for stoichiometric or for catalytic reactions. This CO could react with the intermediates or the products in these reactions.

Introduction

Over many years metal carbene complexes have been used in many selective processes.[1] Most reactions use stable group 6 metal complexes containing alkoxycarbenes (C(OR^1)R^2);[2] others (e.g., for cyclopropanation reactions) use in situ generated metal carbene complexes of nonstabilized carbenes (CR^{1}R^2).[1,3] In the past decade, metal complexes of stable N,N-heterocyclic carbenes (NHCs) have become extremely popular in catalysis.[4] Metal carbene complexes are accessible by a number of methods, including coordination of stable carbenes[4,5] and others.[6] The use of diazo derivatives and transmetalation from other easily prepared metal carbenes[7,8] can be applied to generate carbenes in catalytic cycles. In this context the carbene complexes derived from group 6 carbonyls have been used to synthesize NHC metal carbenes,[9] to prepare palladium monoamino carbenes,[10,11] and to generate unstable Pd alkoxycarbenes.[10,12] Thus, [M(CO)$_5$(carbene)] complexes (M = group 6) have been used by Sierra et al. in Pd-catalyzed reactions[8,13] and by Barluenga and Aumann in Ni-,[14] Rh-,[15] and Cu-catalyzed[15b,16] cyclizations.

In the course of our studies of the migratory insertion reaction in palladium carbenes,[10,11] we attempted to prepare some [PdRX{C(NR$^1{}_2$)R^2}L] (R = Me, Ph) complexes by carbene transmetalation from [W(CO)$_5${C(NR$^1{}_2$)R^2}] and we have found out that carbene transfer occurs concurrently with carbonyl insertion into the Pd−R bond. The increasing use of [M(CO)$_5$-

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* To whom correspondence should be addressed. E-mail: albeniz@qi.uva.es (A.C.A.); espinet@qi.uva.es.

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Scheme 1. Synthesis of Complexes 4−7

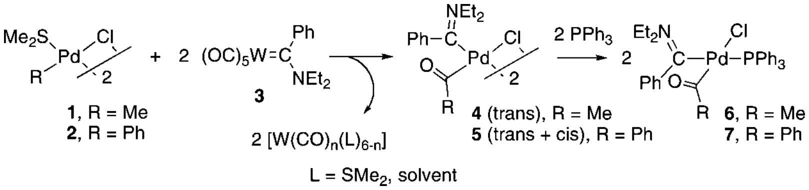

Table 1. Selected Distances (Å) and Angles (deg) for Complexes 4, 5, and 7

	4[a]	5	7
Pd−$C_{carbene}$	2.00(3)	1.976(12)	2.048(8)
Pd−C_{acyl}	2.02(4)	1.978(14)	1.969(9)
Pd−Cl	2.455(11)	2.406(3)	2.438(2)
Pd−P			2.352(2)
$C_{carbene}$−N	1.30(4)	1.298(15)	1.311(10)
C_{acyl}−O	1.16(5)	1.211(16)	1.231(10)
$C_{carbene}$−Pd−C_{acyl}	85.6(13)	88.9(5)	84.8(3)
$C_{carbene}$−Pd−Cl	94.8(9)	93.7(3)	91.2(2)

[a] Average values of both data in the dimer are given.

(carbene)] complexes (M = group 6 metal) in carbene transmetalations, for either stoichiometric or catalytic syntheses, makes it necessary to take this potential complication into account.

Results and Discussion

Reactions of the Me−Pd and Ph−Pd derivatives **1** and **2** with the tungsten carbene complex **3** leads to the dimeric carbene acyl complexes **4** and **5**, respectively (Scheme 1). In addition to the transmetalation of the carbene from W to Pd, an insertion of CO into the Pd−R bond has occurred, so that the initially expected $[Pd_2(\mu\text{-}Cl)_2Me_2\{C(NEt_2)Ph\}_2]$ compound is not obtained. In solution and in the solid state, complex **4** is obtained as a trans isomer, regarding the arrangement of the carbene groups on both sides of the dimer (see below); in solution, complex **5** is a mixture of cis (minor) and trans (major) isomers whose signals partially overlap at room temperature but can be distinguished at 243 K (cis:trans = 1:10). Compounds **4** and **5** can be easily transformed into **6** and **7** by bridge cleavage with PPh_3. The substitution of the bridging chloride occurs trans to the carbene, the ligand with the highest trans effect, as observed before for analogous palladium carbene complexes.[10]

The single crystal X-ray structures of **4**, **5**, and **7** were determined. Table 1 gives a selection of distances and angles, and Figure 1 shows the corresponding ORTEP drawings. Complexes **4** and **5** exhibit a planar structure for the double bridge and a trans arrangement of the two carbene (and the two acyl) ligands in the dimer. In all the complexes the C(O)R moiety lies perpendicular to the palladium coordination plane. The carbene group (defined by the $NC_{carbene}C_{Ph}$ plane) also lies perpendicular to the palladium coordination plane, with bond lengths consistent with a Pd−$C_{carbene}$ single bond (1.976−2.048 Å) and a C=N double bond (1.298−1.311 Å). The double-bond character of the latter is also consistent with an ν(C=N) IR band at ca. 1570 cm^{-1}. Hence, as for other palladium monoamino carbenes synthesized before,[10,11] a bond representation as depicted in Scheme 1 is chosen for the molecule throughout this paper.

The ^{13}C NMR chemical shifts in solution for the carbene carbon are similar to those found for other monoamino carbene complexes of palladium: 230.7 (**4**), and 227.2 (**5**) ppm for the dimeric complexes and somewhat higher values for the phosphino derivatives (245.9 ppm, **6**; 245.6 ppm, **7**). The latter show high values for the $^2J_{P-C}$ coupling constant (102 and 104 Hz) consistent with the trans PPh_3−carbene arrangement found in the solid. The acyl groups show characteristic ^{13}C NMR resonances in the range 242−236 ppm and ν(C=O) IR bands in the range 1670−1630 cm^{-1}.

The ^1H NMR spectral patterns of these complexes in solution are interesting. The monomeric complexes **6** and **7** show, whether at room or at low temperature, just one isomer with diastereotopic methylene hydrogens (one AB system for each of the two inequivalent ethyl groups), consistent with fast rotation of the acyl group and slow rotation of the carbene moiety (fast rotation of both groups should produce equivalence within each methylene group). Similar slow rotation of the carbene ligand has been observed before in $[PdBr(C_6F_5)\{C(NEt_2)Ph\}(PPh_3)]$.[10] For the dimeric complex **4** at room temperature, the ^1H NMR spectrum shows just one species, with equivalent methylene hydrogen atoms within each ethyl group, indicating that, in contrast with the monomeric **6**, the rotation of the carbene moiety is also fast in the dimer.[17] At low temperature, when rotation of the carbene becomes slow, **4** gives rise to two isomeric forms, syn and anti (Scheme 2), depending on whether the carbene substituents are on the same or opposite sides of the Pd coordination plane in the dimer (keep in mind that the acyl group is still rotating quickly). Similar rotation rates are observed for **5**, although in this case a mixture of trans (major) and cis (minor) isomers in the dimer is additionally present at 243 K (cis:trans = 1:10).

Some reactions were monitored by NMR to follow the competition of CO transfer/insertion (insertion is apparently very fast, and carbonyl intermediates of Pd were never detected) and carbene transfer. Figure 2 shows the evolution of the reaction of **1** with an excess of the tungsten carbene **3** (**1**:**3** = 1:6), monitored by ^1H NMR at 263 K in CD_3CN.[18] The disappearance of **1** is accompanied by the appearance of the palladium acyl carbene complex **4** and the palladium acyl complex $[Pd_2(\mu\text{-}Cl)_2(COMe)_2(SMe_2)_2]$ (**8**), along with $[W(CO)_5(SMe_2)]$. Complex **8** is the result of CO transfer and insertion into the Pd−Me bond of **1**; in fact, it was independently synthesized by bubbling CO in a solution of **1**.[19] Complex **4** could be the result of carbene transfer to **8** or the formation of a putative $[Pd_2(\mu\text{-}Cl)_2\text{-}Me_2\{C(NEt_2)Ph\}_2]$ complex (which was never detected),[20]

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[17] The different rates of carbene rotation in the monomeric and the dimeric complexes could be due to the different geometrical constraints in both complexes. However, it looks more likely that the rotation of the carbene in the dimers requires cleavage of at least one of the chloro bridges.

[18] Complex **1** shows a fluxional behavior in CD_3CN solutions. A mixture of three species, but no free SMe_2, was found when **1** was dissolved in CD_3CN and cooled to 233 K. Thus, these species can be tentatively assigned to the three isomers of $[PdClMe(SMe_2)(NCCD_3)]$ (Pd−Me, δ 0.68, 0.53, 0.36). These complexes undergo fast exchange upon warming to give, at 263 K, the average Pd−Me signal shown in Figure 2 and broad SMe_2 resonances around 2.3 ppm. This is not observed for the acyl derivative **8**, which at 233 K in CD_3CN shows only one species with coordinated SMe_2.

[19] **8** was prepared by following the method described for the analogous $[Pd_2(\mu\text{-}Cl)_2(COMe)_2L_2]$ (L = PR_3): Hayashi, Y.; Isobe, K.; Nakamura, Y.; Okeya, S. *J. Organomet. Chem.* **1986**, *310*, 127–134.

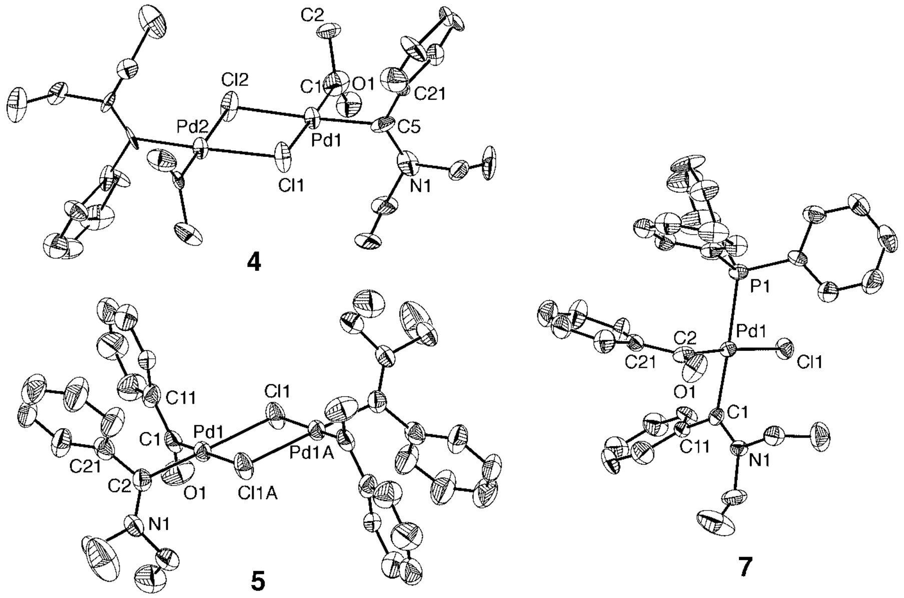
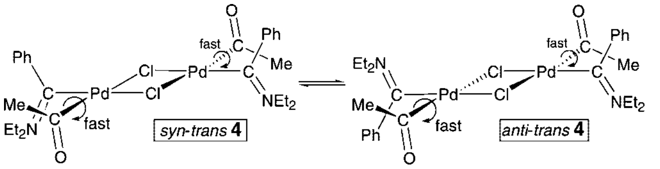


Figure 1. ORTEP drawings for complexes **4**, **5**, and **7** (40% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Scheme 2. Isomers Associated with Slow Carbene Rotation about the Pd−C Bond



which should then undergo fast CO transfer and insertion into the Pd−Me bond as soon as it is formed.

The evolution of the reaction of **1** and **3** could not be quantified, due to severe overlap of the C(O)Me resonance of **8** with SMe_2 signals (Figure 2). However, Figure 3 shows the quantitative results obtained, by ^1H NMR at 273 K, for the reaction of the acyl complex **8** and an excess of $[W(CO)_5\{C(NEt_2)Ph\}]$ (**3**) (**8**:**3** = 1:6, Figure 3a), compared with the reaction of an equimolar mixture of the methyl complex **1** and the acyl derivative **8** with the tungsten carbene (**1**:**8**:**3** = 1:1:6, Figure 3b). The profile of the reaction of **8** with **3**, which corresponds only to carbene transmetalation, shows a steady variation where the decay in the rate of formation of **4** with time is faster than that expected from a first-order dependence on [**4**]. This suggests that part of the SMe_2 liberated in the reaction is not trapped by the $W(CO)_5$ byproduct in the form of $[W(CO)_5(SMe_2)]$ (some $[W(CO)_5(NCCD_3)]$ is also formed, and some decomposition is observed), and is competing with the carbene for the coordination site on Pd, progressively slowing the transmetalation down. For comparison, Figure 3b shows that complex **1** (50% of the starting mixture of Pd compounds, starting at 100 in the graphics) undergoes a fast reaction to give the palladium acyl **8**. This happens with a rate that is faster than the carbene transmetalation to **8** to give **4**, and consequently, an increase in concentration of **8** over the initial value of 100 is observed. The CO transfer/insertion to **1** is fairly fast. When it is complete ($t \approx 200$ min), an amount of **8** equivalent to the initial amount is still unreacted. This, along with the absence of any methylcarbene intermediate and the accumulation of **8** observed in the reaction monitored in Figure 2, support that the CO transfer/insertion is noticeably faster than carbene transmetalation.[21]

A couple of examples of the transfer of a carbene and a CO group that leads to a rhodium[15c] or platinum carbonyl complex have been reported.[9b,d] As far as we know, there is only one report on the formation of palladium acyls by CO transfer from

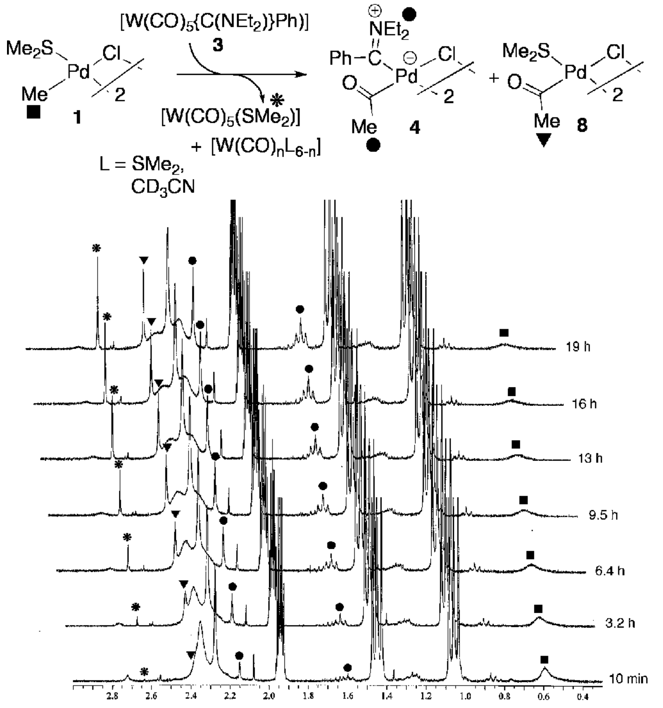


Figure 2. ^1H NMR spectra of the evolution of a mixture of **1** and **3** (1:6) in CD_3CN at 263 K. Signals for unreacted $[W(CO)_5\{C(NEt_2)Ph\}]$, used in excess, and broad signals corresponding to SMe_2 are also seen.

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[20] Reaction mixtures were cooled to 233 K, at different times and conversions, to slow down the exchange process that affects **1**, in order to facilitate the observation of a possible palladium methyl carbene complex. Cooling led to better resolved spectra, but no complex of this type was detected.

[21] We have checked the CO transfer ability of these types of tungsten complexes. $[W(CO)_5(NCMe)]$ reacts with **1** to give **8**, demonstrating that not only **3** but also the reaction byproducts can be the source of CO in the carbonylation. In other words, the carbonylating agent is not necessarily consumed (although its nature changes) as the carbonylation proceeds, this helping to keep the carbonylation rate high.

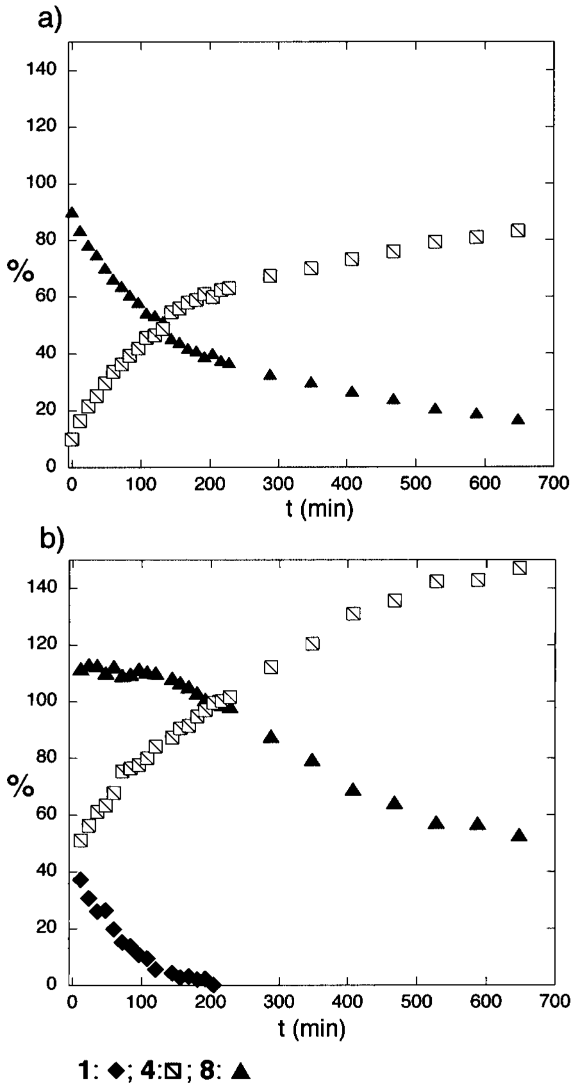

Figure 3. Plots representing the percentage of Pd complexes vs time for the following reactions: (a) **8** and **3** (**8**:**3** = 1:6); (b) a mixture of **1** and **8** with an excess of **3** (**1**:**8**:**3** = 1:1:6). Note that for (a) the maximum production of **4** is 100, whereas that for (b) is 200.

metal carbonyl complexes in the literature.[22] On the basis of theoretical studies on the reaction with cobalt carbonyl complexes, a mechanism was proposed that involves transmetalation of the methyl group from Pd to Co, insertion of CO into the new Co−Me bond, and transmetalation of the acyl group from Co back to Pd. In the reactions reported here, there is no evidence of the formation of a any tungsten acyl in the reactions monitored, starting either from **3** or from $[W(CO)_5(NCMe)]$, and we suggest that simple CO dissociation from **3**, a usual step in most tungsten carbonyl substitution reactions,[23] followed by coordination to Pd and insertion into the Pd−R bond can explain the observed results.

In conclusion, the transfer of CO is a noticeable feature of the transmetalation of carbene described in this work, since the presence of a Pd−R group (R = Me, Ph) leads to a fast CO insertion reaction that alters the nature of the organometallic moiety formed. This complication cannot happen when a Pd−R group is absent (e.g., halide complexes with Pd−X bonds) or when the insertion of CO into the Pd−R bond is thermodynamically disfavored (this is the case for electronegative R groups: e.g., C_6F_5 in our former work, acyls, etc.).[10,11,24] Although in those cases CO transfer may be irrelevant or negligible, the results reported here indicate that, in the transmetalation of carbene moieties from $[W(CO)_5(\text{carbene})]$ complexes, CO is always present as a potential reagent, which can induce unexpected transformations. This should be taken into account when planning stoichiometric or catalytic processes that use this type of carbene source.[8]

Experimental Section

General Considerations. ^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC-300 and ARX-300 spectrometers. Chemical shifts (in δ units, ppm) were referenced to Me_4Si (^1H and ^{13}C), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P). The spectral data were recorded at 293 K unless otherwise noted. IR spectra were recorded on a Perkin-Elmer IR 883 and Perkin-Elmer FT-IR 1720X spectrophotometer. C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyzer.

All the reactions described were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over and distilled from appropriate drying agents under nitrogen, prior to use. Complexes **1**,[25] **3**,[26] *trans*-$[PdCl_2(SMe_2)_2]$,[27] and $[W(CO)_5(MeCN)]$[28] were prepared according to literature methods.

$[Pd(\mu\text{-}Cl)Ph(SMe)_2]_2$ (2). To a solution of *trans*-$[PdCl_2(SMe_2)_2]$ (1.5000 g, 4.973 mmol) in THF (225 mL) at −80 °C under nitrogen was added dropwise over a period of 45 min a solution of ZnPhCl in THF (25 mL), previously prepared from LiPh (1.73 M in Bu_2O, 7.460 mmol) and $ZnCl_2$ (0.64 M in THF, 6.848 mmol) at −80 °C. The orange solution obtained was warmed to −15 °C over a period of 5 h, giving a yellow solution. It was evaporated to dryness at 0 °C, and the residue was extracted with CH_2Cl_2 (25 mL). The filtered CH_2Cl_2 solution was evaporated to dryness at 0 °C, and addition of Et_2O (25 mL) to the residue yielded a white solid, which was filtered, washed with Et_2O (2 × 5 mL), and vacuum-dried. Yield: 0.5315 g (38%). Anal. Calcd for $C_{16}H_{22}Cl_2Pd_2S_2$: C, 34.18; H, 3.95. Found: C, 33.85; H, 3.68. IR (Nujol mull, cm^{-1}): ν(Pd−S) 334 (w); ν(Pd−Cl) 287 (m), 249 (w). ^1H NMR (300 MHz, δ, $CDCl_3$): 7.15 (m, 2H; H_{ortho} Ph), 7.00−6.85 (m, 3H; H_{para}, H_{meta} Ph), 2.18 (s, 6H; SMe_2). $^{13}C\{^1H\}$ NMR (74.5 MHz, δ, $CDCl_3$, 253 K): 142.9 (s, C_{ipso} Ph), 133.8 (C_{meta} Ph), 128.1 (C_{para} Ph), 124.40 (C_{ortho} Ph), 23.2 (s, SMe_2).

***trans*-$[Pd(\mu\text{-}Cl)(COMe)\{C(NEt_2)Ph\}]_2$ (4).** Complex **3** (0.6100 g, 1.257 mmol) was added to a solution of **1** (0.2914 g, 0.629 mmol) in CH_3CN (12 mL) at room temperature. The mixture was stirred for 2 h. The dark solution was filtered through activated carbon and Celite and then concentrated to ca. 6 mL. Et_2O (10 mL) was added to the residue, and the solution was kept at −20 °C for 1 h.

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Table 2. Crystallographic Data for Complexes 4, 5, and 7

	4	5	7
formula	$C_{26}H_{36}Cl_2N_2O_2Pd_2$	$C_{36}H_{40}Cl_2N_2O_2Pd_2$	$C_{36}H_{35}ClNOPPd$
mol wt	692.27	816.40	670.47
cryst color and habit	yellow prism	yellow prism	yellow prism
cryst size (mm)	0.11 × 0.07 × 0.02	0.12 × 0.1 × 0.04	0.18 × 0.09 × 0.04
T (K)	298(2)	298(2)	298(2)
wavelength (Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P1$	$Pbca$	$P2_1/n$
a (Å)	8.109(2)	15.724(4)	10.082(2)
b (Å)	8.126(2)	13.236(3)	33.052(8)
c (Å)	12.537(4)	16.927(4)	10.983(3)
α (deg)	102.591(5)	90	90
β (deg)	101.595(5)	90	116.573(4)
γ (deg)	109.386(5)	90	90
V (Å^3)	726.3(4)	3523.0(15)	3273.3(14)
Z	1	4	4
D_{calcd} (g cm^{-3})	1.583	1.539	1.361
μ (mm^{-1})	1.446	1.206	0.725
no. of collected rflns	6926	30475	32993
scan range (θ) (deg)	$1.74 \leq \theta \leq 28.34$	$2.34 \leq \theta \leq 26.39$	$1.23 \leq \theta \leq 24.71$
no. of unique rflns (R_{int})	3539 (0.0618)	3608 (0.2266)	5687 (0.1568)
no. of rflns ($I > 2\sigma(I)$)	2684	1675	3074
no. of params	308	201	372
final R indices^a ($I > 2\sigma(I)$)	R1 = 0.0735	R1 = 0.0852	R1 = 0.0595
	wR2 = 0.1971	wR2 = 0.1811	wR2 = 0.1345
R indices^a (all data)	R1 = 0.0958	R1 = 0.1976	R1 = 0.1407
	wR2 = 0.2138	wR2 = 0.2492	wR2 = 0.1905
largest diff peak, hole (e Å^{-3})	1.501, −1.049	1.438, −1.129	0.745, −1.048

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|)$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

A grayish solid was obtained, which was filtered, washed with *n*-hexane (2 × 5 mL), and air-dried. Yield: 0.2436 g (65%). Recrystallization of a small portion of this solid from a CH_2Cl_2/Et_2O solution at −20 °C, previous disolution of the solid in CH_2Cl_2, and filtration through activated carbon and Celite yielded yellow crystals suitable for X-ray diffraction studies and elemental analyses. Anal. Calcd for $C_{26}H_{36}Cl_2N_2O_2Pd_2$: C, 45.10; H, 5.25; N, 4.04. Found: C, 44.81; H, 4.88; N, 4.08. IR (Nujol mull, cm^{-1}): ν(C═O) 1674 (m), 1652 (m); ν(C═N) 1596 (w), 1570 (m); ν(Pd−Cl$_{bridging}$) 275 (w). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 7.39 (m, 2H; H$_{meta}$ Ph), 7.28 (m, 1H; H$_{para}$ Ph), 6.95 (m, 2H; H$_{ortho}$ Ph), 4.90 (m, 2H; C*H*$_2$), 3.41 (m, J = 14.5, 7.0 Hz, 2H; CH′$_2$), 2.23 (s, 3H; C(O)Me), 1.69 (t, J = 7.0 Hz, 3H; CH$_3$), 1.11 (t, J = 7.0 Hz, 3H; CH′$_3$). ^{13}C{^{1}H} NMR (74.5 MHz, δ, $CDCl_3$): 241.5 (s, *C*(O)Me), 228.4 (s, Pd−C$_{carbene}$), 143.0 (s, C$_{ipso}$ Ph), 128.4 (s, C$_{meta}$ Ph), 127.0 (s, C$_{para}$ Ph), 121.3 (s, C$_{ortho}$ Ph), 56.1 (s, *C*H$_2$), 47.0 (s, C′H$_2$), 37.5 (s, C(O)*Me*), 13.9 (s, CH$_3$, C′H$_3$).

[Pd(*μ*-Cl)(COPh){C(NEt$_2$)Ph}]$_2$ (5). To a solution of **3** (0.2130 g, 0.439 mmol) in CH_3CN (20 mL) was added **2** (0.1234 g, 0.219 mmol) at room temperature. The mixture was stirred for 5 h. The dark solution was filtered through activated carbon and Celite and then evaporated to dryness. EtOH (20 mL) was added to the residue, and the solution was kept at −20 °C for 30 min. A dark greenish solid was obtained, which was filtered, washed with Et_2O (2 × 5 mL), and air-dried. Yield: 0.1056 g (59%). Recrystallization of this solid from CH_2Cl_2/Et_2O solution at −20 °C, previous dissolution of the solid in CH_2Cl_2, and filtration through activated carbon and Celite yielded yellow crystals suitable for X-ray diffraction studies and elemental analyses. **5** is a mixture of trans and cis isomers at 293 K (see text). Anal. Calcd for $C_{36}H_{40}Cl_2N_2O_2Pd_2$: C, 52.95; H, 4.95; N, 3.43. Found: C, 52.51; H, 4.86; N, 3.46. IR (Nujol mull, cm^{-1}): ν(C═O) 1644 (m); ν(C═N) 1588 (w), 1576 (m), 1562 (m); ν(Pd−Cl) 272 (w). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 8.06 (bm, 2H; H$_{ortho}$ C(O)Ph, cis + trans), 7.55 (bm, H$_{para}$ C(O)Ph, cis), 7.32 (bm, H$_{para}$ C(O)Ph, trans), 7.28−7.05 (ma, 5H; H$_{meta}$ C(O)Ph, H$_{meta}$ Ph, H$_{para}$ Ph, cis + trans), 6.69 (bm, H$_{ortho}$ Ph, cis), 6.63 (bm, H$_{ortho}$ Ph, trans), 5.02 (bm, 2H; CH$_2$, cis + trans), 3.31(bm, 2H; CH′$_2$, cis + trans), 1.70 (bm, 3H; CH$_3$, cis + trans), 0.99 (t, 3H; CH′$_3$ cis + trans). ^{13}C{^{1}H} NMR (74.5 MHz, δ, $CDCl_3$): 240.8 (s, *C*(O)Ph, cis + trans), 226.0 (s, Pd−C$_{carbene}$, cis + trans), 143.0 (s, C$_{ipso}$ Ph, cis + trans), 138.8 (s, C$_{ipso}$ C(O)*Ph*, cis + trans), 131.1 (s, C$_{para}$ C(O)*Ph*, cis + trans), 130.3 (s, C$_{ortho}$ C(O)*Ph*, cis + trans), 128.2 (s, C$_{meta}$ Ph, cis + trans), 127.6 (s, C$_{meta}$ C(O)*Ph*, cis + trans), 126.8 (s, C$_{para}$ Ph, cis + trans), 121.5 (s, C$_{ortho}$ Ph, cis + trans), 55.9 (s, CH$_2$, trans), 55.7 (s, CH$_2$, cis), 47.2 (s, C′H$_2$, cis/trans), 14.0 (s, CH$_3$, C′H$_3$, cis + trans).

[PdCl(COMe){C(NEt$_2$)Ph}(PPh$_3$)] (6). PPh$_3$ (0.0907 g, 0.346 mmol) was added to a solution of **4** (0.1100 g, 0.158 mmol) in CH_2Cl_2 (15 mL) at room temperature. The dark greenish solution was stirred for 30 min and evaporated to dryness. Et_2O (10 mL) was added to the residue, and the solution was kept at −20 °C for 1 h. A grayish solid was obtained, which was filtered, washed with Et_2O (2 × 5 mL), and air-dried. Yield: 0.1678 g (87%). Recrystallization of a small portion of this solid from CH_2Cl_2/Et_2O solution at −20 °C, previous disolution of the solid in CH_2Cl_2, and filtration through activated carbon and Celite yielded yellow crystals suitable for elemental analyses.

Anal. Calcd for $C_{31}H_{33}ClNOPPd$: C, 61.19; H, 5.48; N, 2.30. Found: C, 60.92; H, 5.24; N, 2.46. IR (Nujol mull, cm^{-1}): ν(C═O) 1662 (m), 1647 (m); ν(C═N) 1597 (w), 1578 (m), 1571 (m); ν(Pd−Cl) 331 (w). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 7.65 (m, 6H; PPh$_3$), 7.50−7.29 (m, 14H; PPh$_3$, Ph), 5.00, 4.78 (AB system, J = 12.7, 7.2 Hz, 2H; CH$_2$), 3.59, 3.44 (AB system, J = 12.3, 7.2 Hz, 2H; CH′$_2$), 1.76 (t, J = 7.2 Hz, 3H; CH$_3$), 1.48 (s, 3H; C(O)Me), 1.18 (t, J = 7.2 Hz, 3H; CH′$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, δ, $CDCl_3$): 20.3 (s). ^{13}C{^{1}H} NMR (74.5 MHz, δ, $CDCl_3$, 243 K): 245.9 (d, $^2J_{C,P}$ =102 Hz, Pd−C$_{carbene}$), 242.2 (s, *C*(O)Me), 142.9 (s, C$_{ipso}$ Ph), 134.5 (d, $^2J_{C,P}$ = 12 Hz, C$_{ortho}$ PPh$_3$), 131.5 (d, $^1J_{C,P}$ = 40 Hz, C$_{ipso}$ PPh$_3$), 130.4 (s, C$_{para}$ PPh$_3$), 128.7 (s, C$_{meta}$ Ph), 128.5 (d, $^3J_{C,P}$ = 9 Hz, C$_{meta}$ PPh$_3$), 127.3 (s, C$_{para}$ Ph), 122.4 (s, C$_{ortho}$ Ph), 55.8 (s, CH$_2$), 47.1 (d, $^4J_{C,P}$ = 4.6 Hz, C′H$_2$), 39.5 (d, $^3J_{C,P}$ = 11 Hz, C(O)*Me*), 14.4 (s, CH$_3$), 13.6 (s, C′H$_3$).

[PdCl(COPh){C(NEt$_2$)Ph}(PPh$_3$)] (7). PPh$_3$ (0.0744 g, 0.284 mmol) was added to a solution of **5** (0.1079 g, 0.132 mmol) in CH_2Cl_2 (15 mL) at room temperature. The greenish solution was stirred for 1 h 30 min and evaporated to dryness. *n*-Hexane (10 mL) was added to the residue, and the solution was stirred for 1 h while being kept at −20 °C. A grayish solid was obtained, which was filtered, washed with cold *n*-hexane (2 × 5 mL), and air-dried. Yield: 0.1433 g (81%). Recrystallization of this solid from CH_2Cl_2/Et_2O solution at −20 °C, previous dissolution of the solid in CH_2Cl_2, and filtration through activated carbon and Celite yielded yellow crystals suitable for X-ray diffraction studies and elemental analyses.

Anal. Calcd for $C_{36}H_{35}ClNOPPd$: C, 64.48; H, 5.27; N, 2.09. Found: C, 64.38; H, 4.91; N, 2.00. IR (Nujol mull, cm^{-1}): ν(C=O) 1630 (m); ν(C=N) 1591 (w), 1577 (m), 1571 (m); ν(Pd−Cl) 333 (w). ^{1}H NMR (300 MHz, δ, $CDCl_3$): 7.50 (m, 6H; PPh_3), 7.10−7.40 (17H; PPh_3, C(O)Ph, Ph), 6.85 (m, 2H; H_{ortho} C(O)Ph), 5.17, 4.80 (AB system, J = 12.7, 7.2 Hz, 2H; CH_2), 3.50, 3.38 (AB system, J = 12.7, 7.2 Hz, 2H; CH'_2), 1.77 (t, 3H; CH_3), 1.12 (t, J = 7.2 Hz, 3H; CH'_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, δ, $CDCl_3$): 19.7 (s). $^{13}C\{^1H\}$ NMR (74.5 MHz, δ, $CDCl_3$, 243 K): 245.6 (d, $^2J_{C,P}$ =104 Hz, Pd−$C_{carbene}$), 236.4 (d, $^2J_{C,P}$ = 4.5 Hz, *C*(O)Ph), 143.1 (s, C_{ipso} Ph), 139.8 (d, $^3J_{C,P}$ = 7.5 Hz, C_{ipso} C(O)*Ph*), 134.4 (d, $^3J_{C,P}$ = 12 Hz, C_{ortho} PPh_3), 131.3 (d, $^1J_{C,P}$ = 41 Hz, C_{ipso} PPh_3), 130.8 (s, C_{para} C(O)*Ph*), 130.0 (s, C_{para} PPh_3, C_{ortho} C(O)*Ph*), 128.2 (s, C_{meta} Ph), 128.1 (d, $^3J_{C,P}$ = 10.5 Hz, C_{meta} PPh_3), 127.1 (s, C_{meta} C(O)*Ph*), 126.8 (s, C_{para} Ph), 55.1 (s, CH_2), 47.2 (d, $^4J_{C,P}$ = 4.5 Hz, $C'H_2$), 14.3 (s, CH_3), 13.6 (s, $C'H_3$).

X-ray Crystal Structure Determinations. Crystals suitable for X-ray analyses were obtained by slow diffusion of *n*-hexane (**4**) or Et_2O (**5**, **7**) into a solution of the complex in CH_2Cl_2 at −20 °C. Each crystal was mounted on the tip of a glass fiber. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo Kα radiation (0.710 73 Å). The reflections were collected, the intensities were integrated, and the structures were solved by direct methods procedures.[29] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Relevant crystallographic data are collected in Table 2.

Followup of the Reactions by NMR Reaction of 1 and 3. A 5 mm NMR tube was charged with **1** (0.0020 g, 0.005 mmol), **3** (0.0133 g, 0.027 mmol), and CD_3CN (0.6 mL), under nitrogen at −30 °C. The solution was then monitored by ^{1}H NMR spectroscopy at 263 K. The resulting products were identified as **4**, **8**, and $[W(CO)_5(SMe_2)]$. The same sample was warmed to room temperature and the complete disappearance of **8**, to form **4** was observed.

8: ^{1}H NMR (300 MHz, δ, $CDCl_3$/CD_3CN) 2.48/2.41 (s, 3H; Me), 2.38/2.31 (s, 6H; SMe_2).

$[W(CO)_5(SMe_2)]$: ^{1}H NMR (300 MHz, δ, CD_3CN) 2.65 (s, 6H; SMe_2).

The reactions of a mixture of **1** + **8** + **3** or **8** + **3**, in the starting molar ratios given in the text, were carried out by following the same procedure, but the followup was carried out at 273 K.

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Supporting Information Available: Figures showing ^{1}H NMR spectra of **4** and **5**, as well as NMR data at different temperatures, and CIF files giving complete crystallographic data for complexes **4**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Data analysis and drawing were performed with the programs SMART V5.051 (1998), SAINT V6.02 (1999), and: Sheldrick, G. M. SHELXTL V5.1; Bruker AXS, Inc., Madison, WI, 1998.