Rh–O and Rh–C features for the Rh–carbonyl ligands. Thus, it appears that, in the adsorption process, most if not all of the Rh–Cl bonds are lost for the olefin complexes, while some are retained in the case of the carbonyl species.[25]

The most interesting observation in the EXAFS data is seen in the ethylene sample **1a** which has been exposed to carbon monoxide. The resulting sample gives rise to an EXAFS spectrum (Figure 2C) which is virtually identical to that for the CO complex adsorbed directly, **3a** (Figure 2D)—*including the Rh–Cl feature missing in the original ethylene sample.* The exchange reaction involves not only the quantitative replacement of the ethylene ligands bound to the Rh center but also re-formation of at least some of the Rh–Cl bonds which were lost in the initial adsorption process. The reversible disruption of the Rh–Cl bonds upon chemisorption can be rationalized in terms of the relative π-acid characteristics of the carbonyl and ethylene ligands. Chloride is a stronger π-base than the oxygen-based functionality found on the surface. Consequently, with carbonyl ligands, some Rh–Cl bonds remain upon chemisorption whereas all Rh–Cl bonds break when the ligands are either ethylene or cod. The fact that the disruption of the Rh–Cl bond is reversible indicates that the chloride from a broken Rh–Cl bond remains in close proximity to the rhodium atom and is available for bonding as soon as the π-acidity of the terminal ligand favors it over the competing oxide.

The present results differ from previously described systems in two important aspects. Other procedures for producing highly dispersed rhodium give rise to oxide-bound rhodium centers,[7] and little is known about the influence of ancillary ligands on metal–surface interactions. We have shown here that a different starting material and adsorption procedure gives rise to a significant number of the immobilized $Rh(CO)_2$ centers which have chloride as a directly bound ligand. Second, changes in the relative donor–acceptor abilities of the organic ligands can cause changes in metal support interactions. Specifically, chloride is reintroduced into the rhodium coordination sphere when the π-acid character of the organic ligand increases. Studies to determine the effects of other ligands such as phosphines and phosphites on the surface interactions between rhodium and alumina are in progress.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (Grant CHE 8921632) (P.D.E.) and the donors of the Petroleum Research Fund, administered by the Americal Chemical Society (C.E.B.). Acknowledgment is also made to the Johnson Matthey Corp. for the generous loan of rhodium chloride starting materials. XAS spectra were measured at the Stanford Synchrotron Radiation Laboratory, which is supported by the U.S. Department of Energy and by the NIH Research Resource.

(25) The presence of a small population of dinuclear clusters in the adsorbed samples is difficult to exclude, since the Rh–Rh EXAFS is weak at room temperature and, in the case of **3a**, is perturbed by the Rh–O EXAFS. Cryogenic measurements designed to address this question are in progress.

(26) Earl, W. L.; Vanderhart, D. L. *J. Magn. Reson.* **1982**, *48*, 35.

Articles

The Concept of Geometrical Rigidity around a Transition-Metal Center, a Significant Factor in Improving Thermal Stability for σ-Alkyl Transition-Metal Complexes

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Some four-membered cyclic (σ-alkylamino)palladium complexes containing conformationally free β-hydrogens have been prepared and show a thermal stability that seems hard to explain in traditional terms. However, their relative stabilities correlate with the extent that geometrical rigidity around the metal center is maintained by the ligands. This concept of geometrical rigidity around the metal center is also suggested to be effective as a stabilizing factor for some representative σ-alkyl transition-metal complexes extracted from the literature. At 20 °C the (σ-alkyl)palladium complexes undergo a slow β-hydride elimination and a reinsertion to afford five-membered palladacycles. Attempts to prepare acyclic σ-alkyl complexes from the four-membered cyclic palladium compounds by treatment with trifluoroacetic acid led to decomposition and the formation in good yield of 3-(*N*,*N*-dimethylamino)-1-butene, the expected product from a regioselective β-hydride elimination.

Introduction

Transition-metal-catalyzed reactions frequently involve σ-alkyl intermediates. In most cases the chemistry of these σ-alkyl intermediates constitutes the scope and limitation of the catalysis. This crucial dependence of σ-alkyl complex chemistry is apparent in a wide range of catalytic reactions spanning from strategic scale operations such as polymerization of alkenes down to laboratory scale cross-coupling reactions between alkyl main-group metals and, for example, organic halides (vide infra). A better understanding of the chemistry of σ-alkyl transition-metal complexes is therefore frequently linked to a better un-

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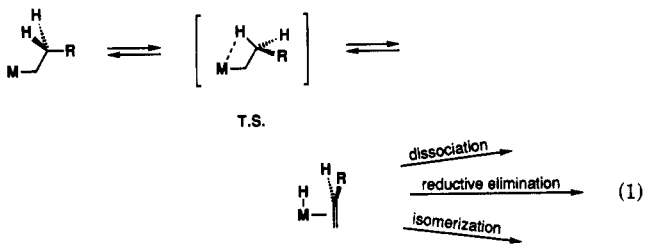
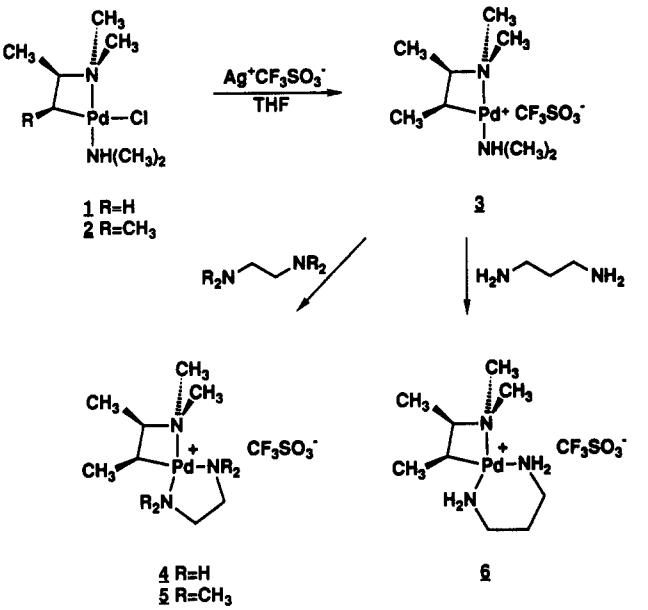
derstanding of catalysis with transition metals. This link is very noticeable when discussing the *limitations* of catalytic reactions. Often, σ-alkyl transition metals are labile. In particular, thermal lability is expected if a σ-alkyl complex carries conformationally free β-hydrogens, which can take part in a β-hydride elimination.[1-4] This step is commonly followed by dissociation or other unwanted reactions (see eq 1). Such destructive sequences (in the following referred to as β-decomposition) commonly restrict the choice of substrates in transition-metal-catalyzed reactions.



(1)

In a previous publication we presented some new four-membered cyclic (σ-alkyl)palladium compounds, **1**, **2**, and cationic **3**.[5] These complexes in crystalline form were surprisingly stable, and the conformationally free β-hydrogens (as in **2** and **3**) did not imply increased thermal lability. In the beginning this stability appeared hard to explain, since our complexes lacked all the characteristics that organometallic tradition normally associates with improved thermal stability.[6-8] We therefore searched for a stabilizing factor so far overlooked, which at the same time would be a common denominator of these complexes.

Scheme I



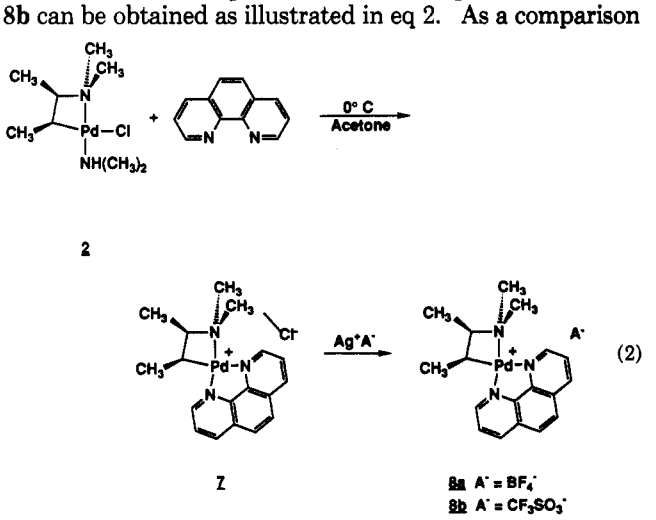
It occurred to us that the stability order related to the resistance the four-membered ring showed against ring opening. We suggested that the small, nonflexible ring is enforcing a *geometrical rigidity around the metal center* (i.e. by keeping the C–Pd–N angle in the metallacycle constant) and this constraint is the factor responsible for stability, possibly by disfavoring a reorganization of the metal orbitals, which is necessary for a β-hydride elimination.

We now provide further support for this concept of geometrical rigidity around the metal center as a stabilizing element and also show that β-decomposition indeed takes place when the rigid four-membered ring is opened. We also present a ring-enlargement reaction, which is the result of a slow β-elimination and reinsertion.

Results

Complex **2**, which is stable for at least 1 h at room temperature (20 °C) in crystalline form, is less stable in solution (vide infra); however, at 0 °C the stability is sufficient for all practical purposes and **2** can be smoothly transformed into cationic **3**. Ligand exchanges with diamines afford, from **3**, the bicyclic compounds **4–6** (see Scheme I). These bicyclic complexes all show improved thermal stability and are perfectly stable in crystalline form at room temperature (20 °C) for considerable time.

Even more stable phenanthroline complexes **7**, **8a**, and **8b** can be obtained as illustrated in eq 2. As a comparison



(2)

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 383. (b) Cross, R. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley & Sons Ltd: New York, 1985; Vol. 2, Chapter 8.

(2) If β-hydrogens are present (and may adopt a cisoid conformation with the metal), the expected decomposition path involves β-hydride elimination, but there are exceptions. For the first example, where α-hydride elimination has preference over β-hydride elimination, see: Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.

(3) Under oxidative conditions, a manifold of reactivity can successfully compete with β-hydride elimination. Examples may be found in: (a) Bäckvall, J. E. *Acc. Chem. Res.* **1983**, *16*, 335. (b) Heumann, A.; Bäckvall, J. E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 207.

(4) If a σ-alkyl group, besides a β-hydrogen, contains a heteroatom, several competing decomposition paths are possible: (a) Hacksell, U.; Daves, G. D. *Organometallics* **1983**, *2*, 772. (b) Hacksell, U.; Kalinoski, H.; Barovsky, D. F.; Daves, G. D. *Acta Chem. Scand., Ser. B* **1985**, *39*, 469 and references therein. (c) De Renzi, A.; Di Blasio, B.; Panunzi, A.; Pedone, C.; Vitagliano, A. *Gazz. Chim. Ital.* **1976**, *106*, 709. (d) Resa, F.; Orchin, M. *J. Organomet. Chem.* **1976**, *108*, 135. (e) Hallings, D.; Green, M.; Claridge, D. V. *Ibid.* **1973**, *54*, 399.

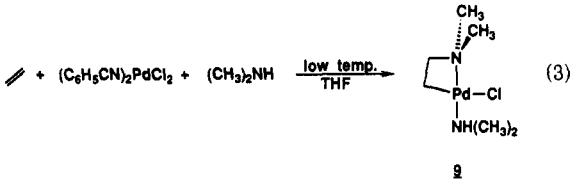
(5) Arnek, R.; Zetterberg, K. *Organometallics* **1987**, *6*, 1230.

(6) A classical way to prepare thermally stable σ-alkyl transition-metal complexes has been to avoid alkyl groups with β-hydrogens (see ref 1b, pp 564). Another accepted method consists of preparing coordinatively saturated σ-alkyl complexes with strongly coordinating ligands. It is assumed that such complexes, prior to dissociation of a ligand, will not easily undergo reactions, which, like the β-hydride elimination, increase the coordination number.

(7) It is well established that stable σ-alkyl complexes can be afforded, where the alkyl group is part of a five-membered (preferentially) or a six-membered (or in rare occasions even a seven-membered) ring. For most of these complexes (in contrast to our complexes) the stability can be rationalized in terms of difficulties to achieve a cisoid conformation between the metal and a β-hydrogen. (a) For a review of cyclometalation of the platinous metals, see: Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451. (b) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(8) The same type of stabilization as in ref 7 against β-hydride elimination of alkoxoplatinum(II) compounds is also recognized. See: Alcock, N. W.; Platt, A. W. G.; Pringle, P. G. *J. Chem. Soc., Dalton Trans.* **1989**, 139 and references therein. In this reference and in ref 7b the stability is explicitly ascribed to the difficulty for the β-hydrogen to adopt a cisoid conformation with the metal.

to these complexes the "parent complex" **9**, of considerably lower stability, was synthesized from ethylene, bis(benzonitrile)dichloropalladium(II), and dimethylamine (see eq 3). The NMR data of the complexes are presented in Table I.

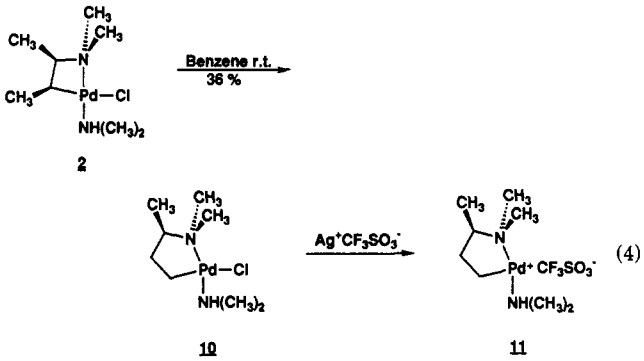


(3)

9

In order to get a better qualitative comparison of thermal stability, all compounds were subjected to controlled heating (see Table II). The following observations may be noted: (1) The "parent compound" **9** is the least stable. (2) The stability is improved if a chelating ligand forms a second metallacycle. (3) If the chelating ligand forms a five-membered ring, this seems slightly more advantageous than if a six-membered ring is formed. (4) Phenanthroline is by far more stability promoting than the other ligands.

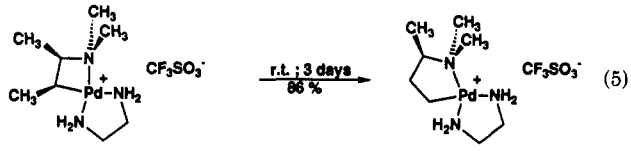
If complex **2** is kept for some hours in benzene solution at 20 °C, decomposition as well as a ring enlargement take place. Some $[(CH_3)_2NH]_2PdCl_2$ is formed, but the main product (36% yield) is the new five-membered cyclic (σ-alkyl)palladium complex **10**, which can be converted into cationic **11** (see eq 4). Similarly, the bicyclic complex **4**



(4)

2 **10** **11**

undergoes ring expansion, however, more slowly (3 days) and more cleanly (86% yield) to afford **12** (eq 5). The new five-membered cyclic complexes appeared to be more robust than the original.



(5)

4 **12**

The structure elucidation is based mainly on NMR spectroscopy (Table III). Two diagnostic changes in the ^{1}H NMR spectrum (compared to the four-membered palladacycle) are the disappearance of one of the methyl doublets and the decreased shift of the lowfield multiplet, the latter being characteristic of the methine proton at carbon 3 in the original complex. DEPT and C–H COSY NMR experiments were used to make assignments of the methylene carbon and their geminal protons possible. (Notice that the high-field methylene protons are connected to the low-field carbon.) NOE difference measurements (see Table IV) confirmed geminal assignments and also made it possible to establish facial relationships between the protons as syn (same side of the ring plane) or anti to the methyl substituent.

When **2** is treated with 2 equiv of trifluoroacetic acid at 0 °C in $CDCl_3$, a rapid decomposition takes place and a palladium mirror appears. After neutralization with sodium carbonate followed by filtration 3-(*N*,*N*-dimethylamino)-1-butene (**13**) is detected (81% yield from **2**) in the ^{1}H NMR spectrum together with some $[(CH_3)_2NH]_2PdCl_2$ (18%). Neither the regioisomer to the allylic amine **13**, 2-(*N*,*N*-dimethylamino)-2-butene nor the hydrolysis product thereof, 2-butanone, could be detected.

This result of a regioselective β-hydride elimination could also be observed when **3** and **4** were treated with trifluoroacetic acid (Table V). On the other hand, the five-membered palladacycle **10** is more reluctant to react.

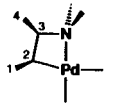
Discussion

The stability properties of the four-membered cyclic complexes, as observed during practical laboratory work, correlate with the phenomenon of *geometrical rigidity around the metal center*, this concept being defined as a reluctance to change one or several bonding angles between the ligands and the metal. Often such a situation with geometrical rigidity is easy to recognize: a bidentate (or tridentate) ligand and the metal form a small ring that will tolerate only minor changes in bonding angles to the metal, as long as the chelate situation is intact. Also a sterically congested situation may imply geometrical rigidity around the metal as long as no crucial metal–ligand bonds are broken. Thus, **2** is *kinetically* stabilized compared to **9**, as a ring opening of **2** will increase repulsive interaction between three cis-positioned methyl groups when the Pd–N bond in the four-membered ring is lengthened (cf. discussion in ref 5). From Table II, one can see that addition of geometrical rigidity around the metal center with a second chelate improves the stability, the smaller the chelate the better (compare complexes **4** and **5** with **6**). The significantly higher stability of **5** compared to **4** may be due to steric effects. The "extra" four methyl groups of **5** may decrease flexibility around palladium. However, in this case the possibility that the increased stability may be of an electronic origin cannot be excluded. It is reasonable to assume that the more basic TMEDA (in **5**) will donate more electron density to the metal than ethylenediamine (in **4**), and this circumstance may retard decomposition. If the second chelate is formed by phenathroline, by far the least flexible of our ligands, superior stability is observed. This property may be a net result of both an expected "rigidity" effect (the N–Pd–N angle in phenanthroline chelate will accept little deviation) as well as hard to assess electronic effects (sp^2-hybridized nitrogen atoms, π-donating and π-accepting properties).

An attractive way to alternatively explain the reluctance of our complexes to undergo β-decomposition might be to consider the "free" β-hydrogens of the complexes to be simply too far away from the metal and, thus, inaccessible for abstraction. In the crystalline state, the distance between the metal and the closest methyl β-hydrogen is slightly above 3 Å in **2**.[5] At approximately 2.5 Å a binding interaction between palladium(II) and an alkyl hydrogen is supposed to be established.[9] Obviously, such an inaccessibility factor may retard a β-elimination. However it cannot be the single reason for the thermal stability, as this factor is rather constant for most of the complexes and, therefore, neither explains the changes in stability of the complexes nor different rates of ring enlargements.

(9) (a) Natile, G.; Gasparrini, F.; Galli, B.; Manatti-Lanfaldi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1980**, *44*, L29. (b) Hosokawa, T.; Ohta, T.; Murahashi, S.; Kido, M. *J. Organomet. Chem.* **1982**, *228*, C55.

Table I. NMR Data for Complexes 2, 4, 5, 6, 7, 8a, 8b, and 9[a]



complex		position 1	2	3	4	$N(CH_3)_2$	ligand
2	^1H	0.74 (d, J = 7.3)	1.27 (dq, J = 8.6, 7.3)	4.17 (dq, J = 8.6, 7.2)	1.00 (d, J = 7.2)	2.59, 2.55	2.56 (d, J = 6.0), 2.54 (d, J = 6.2), 2.66 (br s, N*H*)
	^{13}C	11.82	−3.08	76.12	15.42	50.33, 43.46	42.54, 42.30
4	^1H	0.73 (d, J = 7.3)	1.48 (dq, J = 8.7, 7.3)	4.14 (dq, J = 8.7, 7.1)	1.06 (d, J = 7.1)	2.60, 2.58	2.50–3.05 (CH_2, NH_2, br m)
	^{13}C	12.18	−3.97	76.71	15.84	50.70, 43.96	45.58, 41.95
5	^1H	0.73 (d, J = 7.4)	1.32 (dq, J = 8.8, 7.4)	4.34 (dq, J = 8.8, 7.1)	1.03 (d, J = 7.1)	2.71, 2.70, 2.68, 2.66, 2.64, 2.56	3.02 (1 H, m), 2.75 (1 H, m), 2.41 (2 H, m)
	^{13}C	10.76	2.13	75.60	15.05	52.30, 50.39, 49.32, 49.16, 47.85, 43.77	62.00, 58.11
6	^1H	0.71 (d, J = 7.4)	1.17 (dq, J = 8.7, 7.4)	4.18 (dq, J = 8.7, 7.1)	1.05 (d, J = 7.1)	2.57, 2.53	3.00 (2 H, m), 2.92 (4 H, m, NH_2), 2.55 (2 H, m), 1.76 (2 H, br s)
	^{13}C	11.77	−3.86	76.72	14.73	49.48, 43.33	43.59, 42.98, 28.96
7	^1H	1.11 (d, J = 7.1)	1.98 (dq, J = 8.7, 7.1)	4.66 (dq, J = 8.7, 7.4)	1.26 (d, J = 7.4)	3.00, 2.99	9.02 (1 H, dd, 1.5, 4.8), 8.90 (1 H, dd, 1.4, 5.1), 8.78 (1 H, dd, 1.4, 8.2), 8.76 (1 H, dd, 1.5, 8.2), 8.14 (1 H, d, 9.0), 8.11 (1 H, d, 8.9), 8.02 (1 H, dd, 4.8, 8.0), 7.99 (1 H, dd, 5.1, 8.3)
	^{13}C	11.50	4.28	77.90	15.85	50.43, 44.80	152.18, 151.71, 140.24, 140.13, 128.88, 128.19, 127.10, 127.04
8a	^1H	1.07 (d, J = 7.4)	1.95 (dq, J = 8.7, 7.4)	4.59 (dq, J = 8.7, 7.1)	1.23 (d, J = 7.1)	2.95, 2.94	8.87 (1 H, dd, 1.5, 4.8), 8.81 (1 H, dd, 1.5, 5.1), 8.66 (1 H, dd, 1.5, 8.2), 8.65 (1 H, dd, 1.5, 8.2), 8.08 (1 H, d, 8.9), 8.05 (1 H, d, 8.9), 8.01 (1 H, dd, 4.8, 8.3), 7.94 (1 H, dd, 5.1, 8.2)
	^{13}C	11.10	3.24	76.50	15.42	48.85, 44.26	150.16, 150.01, 139.01, 138.89, 127.72, 127.17, 126.05, 125.61
8b	^1H	0.94 (d, J = 7.4)	1.82 (dq, J = 8.6, 7.4)	4.67 (dq, J = 8.6, 7.2)	1.11 (d, J = 7.2)	2.84, 2.83	8.78 (1 H, dd, 1.5, 4.8), 8.69 (1 H, dd, 1.4, 5.1), 8.55 (1 H, dd, 1.4, 8.4), 8.53 (1 H, dd, 1.5, 8.4), 7.96 (1 H, d, 8.9), 7.93 (1 H, d, 8.9), 7.90 (1 H, dd, 4.8, 8.2), 7.84 (1 H, dd, 5.1, 8.2)
	^{13}C	10.98	3.21	76.46	15.29	49.79, 44.20	150.15, 149.81, 138.97, 138.79, 127.64, 127.16, 125.88, 125.53
9	^1H		0.62 (app t, J = 8.1)	3.98 (app t, J = 8.1)		2.55	2.52 (br d, J = 4.8)
	^{13}C		−18.61	71.86		50.47	42.97

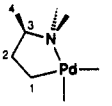
[a] Chloroform-d_1 is used as solvent. J values are in Hz.

Table II. Decomposition Temperatures[a]

complex	decomposn temp, °C	complex	decomposn temp, °C
2	69–70	**8a**	179
3	68	**8b**	149
4	80–85	**9**	<rt[c]
5	108–109[b]	**10**	93–103[b]
6	76–79	**12**	103–112
7	174		

[a] For details, see Experimental Section. [b] Melting and decomposition. [c] The compound immediately turned black at room temperature.

Table III. NMR Data for Complexes 10–12[a]



complex			position 1	2	3	4	$N(CH_3)_2$	ligand
10	^1H	syn	1.47 (ddd, J = 8.9, 5.9, 3.2)	1.29 (dddd, J = 14.0, 11.0, 10.8, 5.9)		0.43 (d, J = 6.6)	2.62; 2.40	2.02 (d, J = 6.2), 1.91 (d, J = 6.2)
		anti	1.74 (ddd, J = 11.0, 8.9, 5.9)	0.75 (dddd, J = 14.0, 5.9, 4.1, 3.2)	2.25 (ddq, J = 10.8, 6.6, 4.1)			3.28 (br s, NH_2)
	^{13}C		23.62	38.07	70.57	10.82	50.26, 42.03	42.53, 42.08
11	^1H	syn	1.71 (ddd, J = 8.9, 5.9, 3.2)	1.50 (dddd, J = 14.0, 11.0, 10.8, 5.9)		1.00 (d, J = 6.6)	2.67, 2.55	2.51 (d, J = 6.1), 2.43 (d, J = 6.1)
		anti	2.07 (ddd, J = 11.0, 8.9, 5.9)	0.85 (dddd, J = 14.0, 5.9, 4.1, 3.2)	2.74 (ddq, J = 10.8, 6.6, 4.1)			
	^{13}C		23.38	38.09	69.73	10.56	49.29, 41.18	42.55, 42.11
12	^1H	syn	1.660 (ddd, J = 9.4, 5.3, 3.1)	1.476 (dddd, J = 14.4, 10.2, 9.6, 5.3)		1.04 (d, J = 6.6)	2.73, 2.61	2.84–2.90 (m, NCH_2)
		anti	1.716 (ddd, J = 9.6, 9.4, 6.3)	1.193 (dddd, J = 14.4, 6.3, 4.1, 3.1)	2.798 (ddq, J = 10.2, 6.6, 4.1)			2.75 (br s, NH_2)
	^{13}C		15.84	36.87	70.46	10.76	50.16, 42.74	45.97, 42.22

[a] The solvents are benzene-d_6 for complex **10** and chloroform-d_1 for **11** and **12**. The ^1H NMR spectra are checked by the simulation-program NMR^{II}, Version 1.0, of Calleo Scientific Software Publishers (1989). Hydrogens situated on the same face of the five-membered ring as the methyl substituent are referred to as syn, the opposite as anti.

Table IV. Observed NOE Enhancement (%) of Complex 10[a]

obsd peaks	irradiated peaks 2.25	1.74	1.47	1.29	0.75	0.43
2.40						2.6
2.25		2.1	2.1		4.3	7.9
1.74			8.6			
1.47		6.9				
1.29			3.3		10.0	
0.75	3.4			10.3		

[a] Solvent is benzene-d_6.

Table V. Yield of Allylic Amine 13[a]

entry	complex	no. of equiv of CF_3CO_2H	temp, °C	yield, %
1	**2**	2	0	81
2	**3**	2	0	22
3	**3**	2	rt	33
4	**3**	2[b]	rt	60
5	**4**	3	0	86
6	**10**	2	rt	7

[a] The reactions are run in chloroform-d_1; yields are measured by NMR spectroscopy. For further details, see the Experimental Section. [b] One equivalent of Bu_3N/CF_3CO_2H is added.

Another potential explanation to stability may be that formation of a three-coordinate complex has to precede a β-hydride elimination. Such a rationale cannot be ruled out and would be consist with some of our observations; e.g., complexes with chelating ligands generally show improved stabilities.

Theoretical calculations support the hypothesis that β-hydride elimination from diethylplatinum(II) complexes preferentially takes place from three-coordinate species.[10] Furthermore, it has been shown that bis(phosphine)dialkylplatinum(II) complexes undergo β-elimination after a rate-determining dissociation of phosphine.[11] However, corresponding (dialkyl)palladium(II) complexes β-eliminate mainly via a nondissociative path.[11a,12] It is also suggested that β-hydride elimination from *cis*-bis(phosphine)alkylplatinum(II) chloride is nondissociative, with dissociation of alkene as the rate-determining step.[13] In our case, the stability in solution is higher for the cationic 14-electron complex **3** than for the neutral 16-electron complex **2**,[5] suggesting that dissociation of an anionic ligand can actually be stabilizing. Neither does it seem that dissociation of a neutral ligand must be a prerequisite for destabilization, as **5**, with a tertiary diamine ligand, is more stable than **4**, with a primary (less basic but more strongly coordinating) diamine ligand.

The β-hydride elimination has often proven to be a reversible step.[11e,14-16] In view of this, the slow ring enlargement (eqs 2 and 3) can be seen as the net result of an initial β-hydride elimination and a final hydride reinsertion, whereby palladium moves to the terminal carbon. Mainly, three thermodynamic factors favor such a ring expansion: (I) the increase in bond strength on going from a secondary carbon- to a primary carbon–palladium bond; (II) the release of ring strain on going from a four- to a five-membered palladacycle; (III) the eventual release of steric repulsion. The preference for a primary (σ-alkyl)-palladium complex over a secondary complex is determined to be 1.6 kcal/mol (at 75 °C) for a sterically unhindered (dialkyldithiocarbamato)palladium complex.[17] Ring strain is assumed to be modest (considerations suggest ≤5 kcal larger for platinacyclobutane than for platinacyclopentane[18]). In our case, also the third term due

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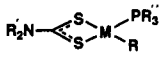
to release of steric repulsion between the cisoid methyl groups will add to this preference. The sum of such rather modestly stabilizing factors may altogether account for the observed increase in stability of the five-membered palladacycles (assuming kinetics correlate with thermodynamics in this case).

Efforts to isolate or observe ring-opened complexes by addition of acid were unsuccessful. Instead, extensive and fast decomposition (black precipitate) was observed, and the regioselective decomposition product, the allylic amine **13**, was usually formed in good yield. The regioselectivity in this β-elimination is consistent with the view that partial positive charge is built up on the β-carbon in the transition state.[14,19] Protonation of the tertiary ring nitrogen would then disfavor abstraction of hydride from the β-methine carbon. Obviously, opening of the ring dramatically destabilizes the system, and β-hydride elimination is in such circumstances the main decomposition path. The initial ring opening appears to be the slow step, at least for the cationic palladium complexes, as room temperature (20 °C) is needed for decomposition of complex **3** (see Table V, entry 4). It is noticeable that, under the same conditions, **3** (see entry 2) gives a lower yield of **13** than **4** (see entry 5). We interpret this observation in terms of rather weakly coordinating trifluoroacetate as an assisting ligand of some importance in the ring-opening process. To mimic the situation whereby **4** has undergone an initial opening of the ethylenediamine chelate, 1 equiv of tributylammonium trifluoroacetate was added to **3**; this increased the rate of the β-decomposition considerably (see entry 4).

General Interpretation. It is our view that the stabilization we observe for our four-membered cyclic (σ-alkyl)palladium species is just a part of a more general phenomenon: *stabilization by geometrical rigidity around a metal center*. If this holds true, not only complexes where the σ-alkyl group is part of a small to medium size ring should be relatively stable (as exemplified by us and others[7]) but also acyclic σ-alkyl transition metals, where the rigidity is introduced by an auxiliary, chelating ligand. According to the literature this is indeed the case. Reger reports unusually stable acyclic σ-alkyl complexes of platinum, **14**,[17,20] and of palladium, **15**.[17] It is stated for

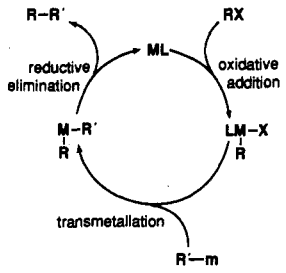


14 M = Pt R = *n*-Pr, *sec*-Pr, *n*-Bu, *sec*-Bu, *t*-Bu, *i*-Bu
15 M = Pd R = *n*-Pr, *sec*-Pr, *n*-Bu, *sec*-Bu, *t*-Bu, *i*-Bu

14 that "these complexes appear to be the most thermally stable simple alkyl derivatives containing β-hydrogen atoms that have been prepared for this metal". We suggest the stability to be caused by the strongly coordinating planar dithiocarbamato ligand, which forms a very rigid four-membered cyclic complex with palladium(II).

The complex (2,2'-bipyridine)diethylpalladium (**16**) has a decomposition (and melting) point at 109 °C.[21] The bipyridine forms a five-membered chelate, and **16** seems to be stabilized both toward β-decomposition and to reductive elimination. Furthermore, bipyridine stabilizes ethyl complexes of nickel, cobalt, and iron.[22] Dimethyl

Scheme II



R and R' = aryl, alkyl
M = Ni, Pd, Rh
m = MgBr, Li, Zn, B, Al, Zr, Hg, Sn
L = usually phosphines

complexes of palladium are strongly stabilized by *N,N,N',N'*-tetramethylethylenediamine (TMEDA) but not by the homologue *N,N,N',N'*-tetramethylpropylenediamine. At lower temperatures TMEDA seems to stabilize methylpalladium(IV) species[23,24] as well as ethylpalladium(II) iodide[24] (in mixtuire with other complexes). Of course, there is a possibility that the thermal stability of the above complexes is merely a result of electronic effects. Strong bonds always thermodymamically stabilize a compound, and sometimes this stability is reflected also in the kinetics. However, we consider it to be more than sheer coincidence that all the compounds mentioned bear this structural element of geometrical rigidity, introduced by a bidentate ligand forming a small metallacycle, in common. The discussed observations raise the question whether a geometrical rigidity around the metal center may suppress more or less all types of reactivity, i.e. not only β-hydride elimination but also reductive elimination. We suggest that the rigidity will suppress more strongly reactions that demand more geometry changes. Thus, the β-hydride elimination, a reaction with an increase in coordination number and considerable geometry change (both in product and in transition state), is strongly hampered. In a reductive elimination the coordination number is decreased, but the geometry of the auxiliary array around the metal does not necessarily have to be changed as much as in a β-hydride elimination (in transition state).

In a general cross-coupling reaction (depicted in a simplified form in Scheme II) the reactivity of the intermediates must be balanced in such a way that β-decomposition and isomerization (due to β-elimination) are minimized but the dialkylmetal intermediate must still undergo reductive elimination. Bidentate phosphines are known to stabilize the σ-alkyl intermediates against β-hydride elimination,[25] and we believe this is, at least in part, a result of these ligands contributing geometrical rigidity to the intermediates. It is noteworthy that in these few cases where β-hydrogen-containing alkyl halides have been successfully used the ligand has always been bidentate.[26-28]

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Concluding Remarks

We see a characteristic pattern for σ-alkyl transition metals that seem to be "unexpectedly" stable against thermal decomposition. This pattern gains extensive support from our own research material and from examples in the literature, and we conclude *geometrical rigidity around a transition-metal center* is a hitherto overlooked phenomenon that is linked to thermal stability for σ-alkyl transition metals. Three points have to be emphasized: (I) *Geometrical rigidity around a transition metal*, defined as a reluctance for the complex to undergo changes of the bonding angles between more or less rigid ligands and the metal, is not the only factor that promotes stability. Electronic factors are obviously important but may be hard to distinguish as purely electronic, as maintained coordination to the metal is a prerequisite for maintained rigidity. (II) The *geometrical rigidity around a transition metal* is just an easy to detect phenomenon, which often *correlates* with thermal stability. We suggest that the actual cause of stability is that a rigid bonding array around the metal will energetically disfavor an orbital reorganization necessary for e.g. a β-hydride elimination. Perhaps this stability criterion can be seen as an analogy to the well-known low reactivity criterion for three- and four-membered cyclic halides in nucleophilic substitution. (III) Factors that commonly are considered destabilizing, such as the presence of conformationally free β-hydrogens in combination with coordinative unsaturation at the metal, do not necessarily overrule this type of stabilization originating from geometrical rigidity.

Finally, it is our hope that awareness of this stabilizing factor may add new rationale to the design of improved catalysts, where σ-alkyl transition metals are crucial intermediates.

Experimental Section

The NMR spectra were recorded on a Bruker Model AM 400 spectrometer. THF was distilled from sodium/benzophenone under nitrogen. *trans*-2-Butene (99%) was purchased from Fluka in tin lecture bottles and used without further purification. Elemental analyses were performed by Mikro-Kemi AB, S-750 19 Uppsala, Sweden, or Analytica AB, S-183 25 Täby, Sweden.

Chloro[2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) (2). This is a slight modification of the procedure in ref 5. Dichlorobis(benzonitrile)palladium(II) (400 mg, 1.04 mmol) was dissolved in 20 mL of THF after degassing under argon at −15 °C. *trans*-2-Butene (4 × 100 mL of gas) was injected from a syringe, and the solution was stirred for 20 min at this temperature. The solution was cooled to −55 to −60 °C. Injection of dimethylamine (2 × 100 mL of gas) from a syringe gave a whitish suspension, which was stirred for 1 h at maintained temperature. After filtration under argon, the filtrate was diluted with 100 mL of pentane and the solution was stored in a freezer (−23 °C) over night for crystallization. The cream white crystals of product **2** (225 mg, 75%) were filtered off and washed with a small amount of pentane.

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*](ethylenediamine)palladium(II) Trifluoromethanesulfonate (4). To a solution of complex **3** [achieved by mixing **2** (28.7 mg, 0.10 mmol) and $AgSO_3CF_3$ (25.7 mg, 0.10 mmol) in THF (5 mL) at 0 °C and filtering off AgCl] was added 6.7 μL (0.1 mmol) of ethylenediamine at 0 °C. The reaction solution was stirred for 10 min whereafter the volume was decreased at 0 °C under vacuum to about 2 mL. Pentane (1 mL) was added, and some colorless crystals appeared. The mixture was stored in a freezer overnight. After filtration product **4** (22 mg, 54%) was obtained as colorless crystals. Anal. Calcd for $C_9H_{22}N_3SO_3F_3Pd$: C, 26.0; H, 5.3; N, 10.1. Found: C, 26.0; H, 5.2; N, 10.1.

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*](*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)palladium(II) Trifluoromethanesulfonate (5). To the solution of complex **3** [achieved by mixing **2** (100 mg, 0.35 mmol) and $AgSO_3CF_3$ (86 mg, 0.35 mmol) in THF (8 mL) at 0 °C and filtering off AgCl] was added TMEDA (40 mg, 0.34 mmol, in 1 mL of THF) at 0 °C. The solution was stirred for 1 h at 0 °C. Addition of 20 mL of pentane caused precipitation of white crystals (126 mg, 71%). The precipitate can be recrystalized from CH_2Cl_2/pentane. Anal. Calcd for $C_{13}H_{31}N_3SO_3F_3Pd$: C, 33.0; H, 6.6; N, 8.9. Found: C, 33.0; H, 6.3; N, 8.9.

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*](1,3-diaminopropane)palladium(II) Trifluoromethanesulfonate (6). To a solution of complex **3** [achieved by mixing **2** (28.7 mg, 0.1 mmol) and $AgSO_3CF_3$ (25.7 mg, 0.1 mmol) in THF (5 mL) at 0 °C and filtering off AgCl] was added 1,3-diaminopropane (16 μL, 14.2 mg, 0.2 mmol). The reaction solution was stirred for 1 h. Evaporation and crystallization from CH_2Cl_2/pentane afforded product **6** (32 mg, 74%) as white crystals. Anal. Calcd for $C_{10}H_{24}N_3PdF_3SO_3$: C, 28.0; H, 5.63; N, 9.78. Found: C, 27.6; H, 5.48; N, 9.64.

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*](phenanthroline)palladium(II) Chloride (7). Complex **2** (50 mg, 0.17 mmol) and phenanthroline monohydrate (34.5 mg, 0.17 mmol) were placed in a flask. After addition of acetone (5 mL) at 0 °C, the reaction mixture was stirred for 10 min and evaporated to dryness to afford product **7** (69 mg, 96%) as yellowish powder. Upon storage this compound partly decomposes via retroamination, probably caused by the coordination ability of the chloride anion.

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*](phenanthroline)palladium(II) Tetrafluoroborate (8a). To a solution of complex **7** prepared from complex **2** (50 mg, 0.17 mmol) and phenanthroline monohydrate (34.5 mg, 0.17 mmol) in a mixed solvent (6 mL) of acetone and nitromethane (1:1) was added $AgBF_4$ (33.1 mg, 0.17 mmol) dissolved in nitromethane (1 mL) at 0 °C. After being stirred for 0.5 h, the mixture was filtered and evaporated to dryness to give **8a** as a yellowish powder (79 mg, 98%). Anal. Calcd for $C_{18}H_{22}N_3BF_4Pd$: C, 45.6; H, 4.68; N, 8.87. Found: C, 45.3; H, 4.43; N, 8.76.

[2-(Dimethylamino)-1-methylpropyl-*C*,*N*](phenanthroline)palladium(II) Trifluoromethanesulfonate (8b). To a solution of complex **7** (42.2 mg, 0.1 mmol) in $CH_2Cl_2/MeNO_2$ (4:1, 5 mL) was added a solution of CF_3SO_3Ag (25.7 mg, 0.1 mmol) in $MeNO_2$ (1 mL) at 0 °C. After being stirred for 0.5 h, the reaction mixture was filtered and evaporated to dryness to give **8b** (44 mg, 82%) as a yellowish powder. Anal. Calcd for $C_{19}H_{22}N_3F_3SO_3Pd$: C, 42.6; H, 4.1; N, 7.8. Found: C, 42.6; H, 4.1; N, 7.6.

Chloro[2-(dimethylamino)ethyl-*C*,*N*](dimethylamine)palladium(II) (9). Into a solution of $Pd(PhCN)_2Cl_2$ (200 mg, 0.52 mmol) in THF (15 mL) at −20 °C was injected ethylene (100 mL of gas, about 4.5 mmol), and the solution was stirred for 10 min. The solution was cooled down to −60 °C, and Me_2NH (100 mL of gas, about 4.5 mmol) was injected. The reaction mixture was stirred, and the temperature was allowed to rise gradually to −40 °C in about 2 h. Then the mixture was stirred for 10 min at 0 °C and filtered. Pentane (40 mL) was added into the filtrate at −60 °C, and the suspension was stirred for 10 min at this temperature. Filtration gave product **9** as a gray-white powder (101 mg, 78%).

Chloro[3-(dimethylamino)butyl-*C*,*N*](dimethylamine)palladium(II) (10). Complex **2** (225 mg) was dissolved in benzene (5 mL) and stirred at room temperature for 3 h. After filtration, the solution was slowly diluted with pentane until some precipitate appeared. The mixture was left at room temperature for another 1 h and filtered once more, and pentane (3 mL) was added to the filtrate. The solution was kept first in a refrigerator (5 °C) overnight and then in a freezer (−23 °C) overnight. Filtering gave a first crop of product (66 mg). Pentane (1 mL) was added into the mother liquid, and the solution was stored in a freezer once more to give the second crop (14 mg) of product **10** affording a total yield of 36%. Anal. Calcd for $C_8H_{21}N_2ClPd$: C, 33.5; H,

(27) {1-[1-(Dimethylamino)ethyl]-2-(phenylthio)ferrocene}- and {1-[1-(dimethylamino)ethyl]-2-(phenylseleno)ferrocene}palladium dichloride complexes couple 1-phenylethyl chloride and allyl Grignards: Honeychuck, R. V.; Okoroafer, M. O.; Shen, L.-H.; Brubaker, C. H. *Organometallics* **1986**, *5*, 482.

(28) With (2,2′-bipyridine)diethylpalladium(II) as catalyst, fumaronitrile has to be added to afford reductive elimination. With this system tetramethyltin can be coupled with 1-phenylethyl bromide: Sustmann, R.; Lau, J.; Zipp, M. *Tetrahedron Lett.* **1986**, *43*, 5207.

7.4; N, 9.8. Found: C, 33.6; H, 7.2; N, 9.7.

[3-(Dimethylamino)butyl-*C*,*N*](dimethylamine)palladium(II) Trifluoromethanesulfonate (11). To a solution of complex **10** (10 mg, 0.035 mmol) in 3 mL of THF was added a solution of CF_3SO_3Ag (9 mg, 0.035 mmol) in 1 mL of THF at 0 °C under argon. After being stirred for 0.5 h, the solution was filtered and evaporated to give **11** (13 mg, 95%) as a pale yellowish oil.

[3-(Dimethylamino)butyl-*C*,*N*](ethylenediamine)palladium(II) Trifluoromethanesulfonate (12). Complex **4** (15 mg, 0.036 mmol) was dissolved in $CHCl_3$ (5 mL) and left at room temperature for 3 days. After filtration the solvent was removed under reduced pressure to give a crude product (14 mg). Crystallization from CH_2Cl_2/pentane afforded white crystals of product **12** (12 mg, 80%). Anal. Calcd for $C_9H_{22}N_3SO_3F_3Pd$: C, 26.0; H, 5.33; N, 10.1. Found: C, 25.4; H, 5.26; N, 10.1.

Decomposition of Palladium Complexes with Trifluoroacetic Acid. (1) Decomposition of Chloro[2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) (2) with Trifluoroacetic Acid. To a solution of complex **2** (28.7 mg, 0.1 mmol) in $CDCl_3$ (1 mL) was added trifluoroacetic acid (15 μL, 0.2 mmol) at 0–5 °C after degassing under argon. The cold bath was removed, and the reaction mixture was stirred for 0.5 h at room temperature. After addition of Na_2CO_3 (23 mg, 0.22 mmol) and stirring for 2 h, the reaction mixture was filtered. Benzene (4.4 μL, 0.05 mmol) was added into the filtrate as an internal NMR standard. On the basis of ^1H NMR and ^{13}C NMR spectra, the products were assigned as 3-(*N*,*N*-dimethylamino)-1-butene (**13**) (81%) and dichlorobis(dimethylamino)palladium (18%). ^1H NMR ($CDCl_3$) of 3-(dimethylamino)-1-butene: δ 1.36 (d, J = 6.8 Hz, 3 H, CH_3), 2.58 (s, 3 H, N-CH_3), 2.61 (s, 3 H, N-CH_3), 3.69 (dq, J_1 = 6.8, J_2 = 8.1 Hz, 1 H, CH-N), 5.37 (dt, J_1 = 17.0, J_2 = 0.8 Hz, 1 H, C=CH_Z), 5.43 (dt, J_1 = 10.4, J_2 = 0.8 Hz, 1 H, C=CH_E), 5.77 (ddd, J_1 = 8.1, J_2 = 10.4, J_3 = 17.0 Hz, 1 H, C=CH-C). ^{13}C NMR of 3-(*N*,*N*-dimethylamino)-1-butene: δ 15.22, 34.68, 42.11, 63.69, 123.81, 130.84. ^1H NMR ($CDCl_3$) of dichlorobis(dimethylamino)palladium: δ 2.38 (d, J = 6.1 Hz, 6 H). ^{13}C NMR of dichlorobis(dimethylamino)-palladium: δ 42.11.

(2) Decomposition of Other Compounds. The compounds [2-(dimethylamino)-1-methylpropyl-*C*,*N*](ethylenediamine)palladium(II) trifluoromethanesulfonate (**4**), chloro[3-(dimethylamino)butyl-*C*,*N*](dimethylamine)palladium(II) (**10**), and [2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) trifluoromethanesulfonate (**3**) were subjected to the same procedure as the decomposition of chloro[2-(dimethylamino)-1-methylpropyl-*C*,*N*](dimethylamine)palladium(II) (**2**) above. For results, see Table V.

Determination of Decomposition Temperatures of Palladium Complexes 2, 4, 5, 6, 7, 8a, 8b, 9, 10, and 12. Decompositon temperature was measured on a Büchi 510 melting point apparatus in an open capillary. The starting temperature was 20 °C and the heating rate was 2 °C/min in all cases. The results are listed in Table II. Compound **9** turned dark before any heating could be applied.

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Reaction of 1-Silyl Dienol Silyl Ethers with Palladium(II) Complexes: Novel Formation of Several Types of (η^3-Allyl)palladium(II) Complexes via the Versatile Complex (η^3-1-(Silylcarbonyl)allyl)palladium Chloride

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Reaction of the 1-silyl dienol silyl ethers **1** with Pd(II) salts gave various (η^3-allyl)palladium complexes depending on the type of Pd(II) salts, solvents, and the acidity of the medium. Treatment of **1** with Li_2PdCl_4 in the presence of Li_2CO_3 in MeOH resulted in simple transmetalation to give the (η^3-1-(silylcarbonyl)-allyl)palladium chloride compound **2**. Reaction of **1** with $PdCl_2(PhCN)_2$ in benzene led to formation of the (η^3-1-silylallyl)palladium chloride compound **4**, a formal decarbonylation product of **2**. Reaction of **1** with $PdCl_2(PhCN)_2$ in MeOH gave the (η^3-1-methoxy-3-methyl-1-silylallyl)palladium chloride compound **5**. The key complex **2** was transformed into **4** by decarbonylation or into **5** by two-electron reduction. The complex **2** afforded (η^3-1-(methoxycarbonyl)allyl)palladium chloride (**3**) when treated with a stoichiometric amount of $PdCl_2(PhCN)_2$ in MeOH in the presence of Li_2CO_3 and also the (η^3-1-methoxy-3-(methoxymethyl)-1-silylallyl)palladium chloride compound **8** on treatment with a catalytic amount of HCl in MeOH. Possible reaction sequences connecting all of these η^3-allyl complexes are proposed.

Introduction

Extensive studies have been done on the reactions of (η^3-allyl)metal complexes.[1] In contrast, however, the chemistry of the (η^3-allyl)metal complexes in which a functional group is attached to the allyl moiety still remains to be studied. In view of this, the studies on the carbonyl groups attached at terminal carbons of an η^3-allyl system are very interesting. However, there have been only a few examples of the utilization of such carbonyl groups, i.e. those in (η^3-allyl)molybdenum[2] and (η^3-allyl)ruthenium complexes.[3] No such utilization in (η^3-allyl)palladium has yet been reported.

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