

Reversible carbonylation of cationic palladium 2,6-bis[(dimethylamino)methyl]pyridine complexes: the first X-ray structure of a cationic acyl-palladium complex

Bertus A. Markies[†], Peter Wijkens[†], Jaap Boersma^{*,†}, Anthony L. Spek[‡] and Gerard van Koten[†]

[†] Debye Research Institute, Department of Metal-Mediated Synthesis, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

[‡] Laboratory of Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

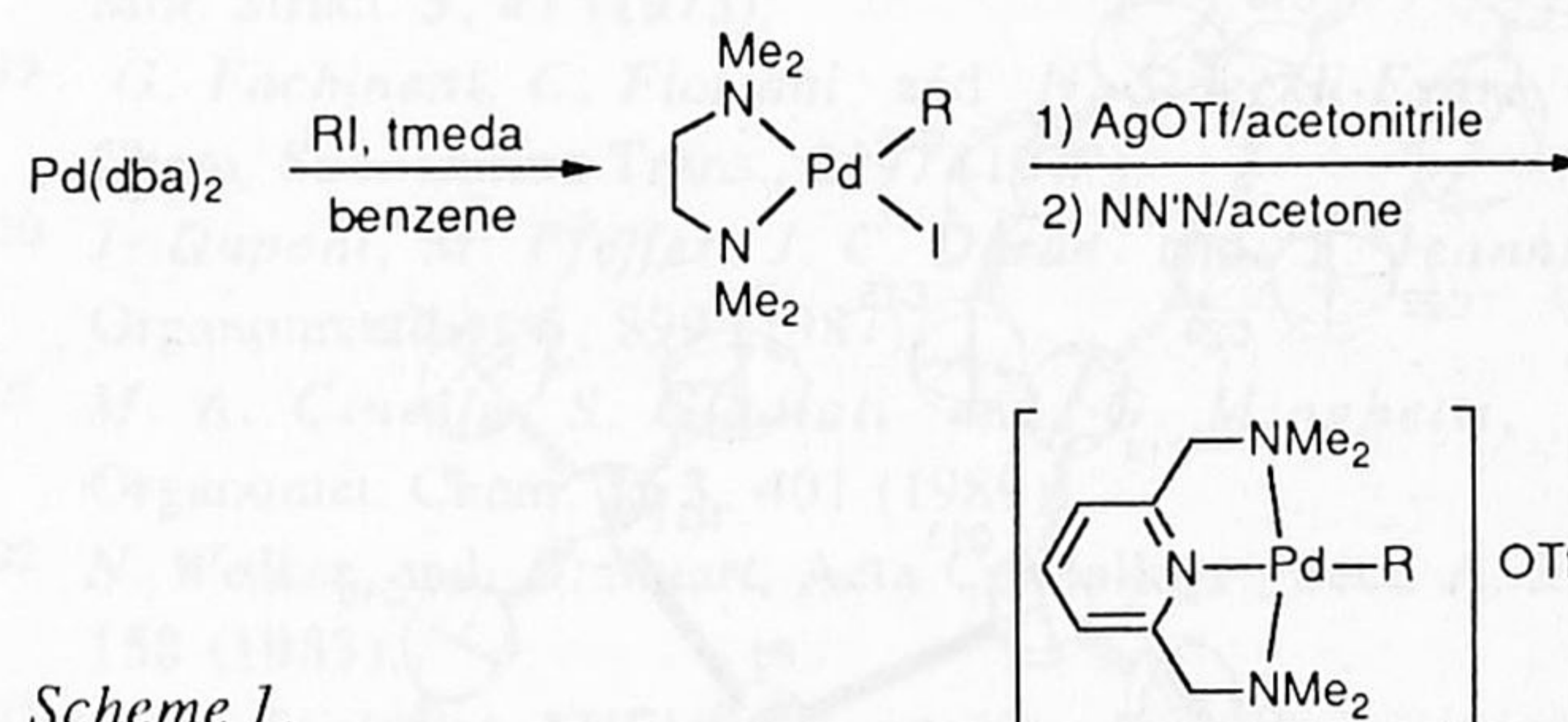
(Received February 19th, 1991)

Abstract. (1-Naphthyl){2,6-bis[(dimethylamino)methyl]pyridine}palladium(II) trifluoromethanesulphonate (**1b**, [Pd(1-C₁₀H₇)(NN'N)]OTf) was prepared in 60% yield starting from bis(dibenzylideneacetone)palladium(0) (Pd(dba)₂) and 1-iodonaphthalene. (1-Naphthoyl){2,6-bis[(dimethylamino)methyl]pyridine}palladium(II) trifluoromethanesulphonate (**2b**, [Pd(C(O)-1-C₁₀H₇)(NN'N)]OTf), characterized by X-ray crystallography, was obtained by insertion of carbon monoxide into the palladium-carbon bond of **1b** in acetone solution. This insertion process was shown to be reversible.

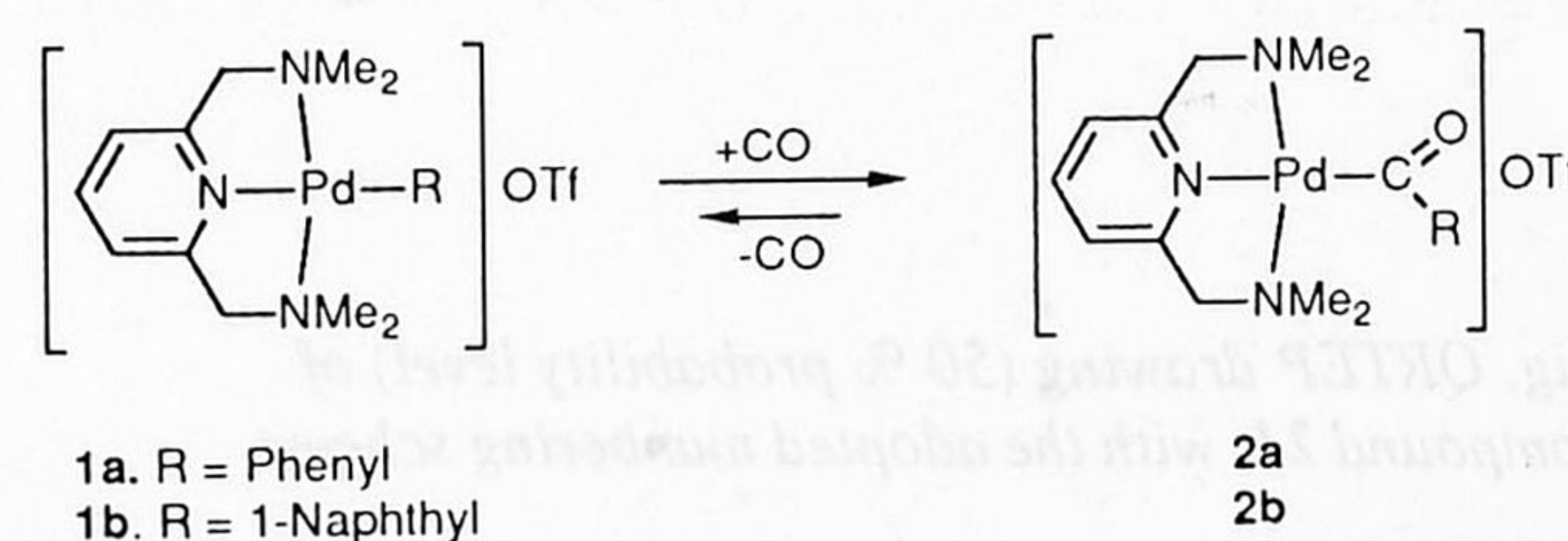
Insertion of carbon monoxide into metal-carbon bonds is a key process with widespread applications in homogeneous catalysis with organometallic compounds.¹⁻³ The insertion process for four-coordinate d⁸ transition-metal compounds with monodentate ligands is generally assumed to follow either a dissociative or an associative route depending on the base strength of the ligands. Complexes with strongly basic ligands favour insertion from five-coordinate species, while the complexes with less basic ligands prefer the dissociative route. To provide evidence for these mechanisms, extensive kinetic studies in solution by spectroscopic methods have been carried out.⁴⁻⁶ For complexes with chelating ligands the insertion mechanism of carbon monoxide is not clear. In most cases a weakly coordinating chelating ligand seems to be required to allow insertion. It is, however, unknown if insertion of carbon monoxide from five-coordinate species can take place for chelate compounds.

Solid state structural studies of palladium-acyl complexes are very limited due to the instability of most acyl complexes towards deinsertion of carbon monoxide. All known structures are of neutral compounds, such as *trans*-PdCl(C(O)C(O)OMe)(PPh₃)₂⁷ and *trans*-PdCl(*n*-heptanoyl)(PPh₃)₂,⁹ which bear monodentate phosphorus ligands.⁷⁻¹¹ In this report we present the results of the first detailed structural study of a cationic palladium-acyl complex. This compound [Pd(C(O)-1-C₁₀H₇)(NN'N)]OTf (**2b**) bears the new neutral, terdentate amine ligand 2,6-bis[(dimethylamino)methyl]pyridine (NN'N).

Recently we synthesized a new class of cationic mono-organopalladium(II) complexes with the general formula [PdR(NN'N)]OTf. We obtained the phenyl¹² (**1a**, 85%) and 1-naphthyl¹³ compounds (**1b**, 60%) as yellow crystalline materials by the route outlined in Scheme 1. The aryl



compounds **1a** (R = phenyl) and **1b** (R = 1-naphthyl) show reversible insertion of carbon monoxide.



The reaction of **1b** with carbon monoxide (1 atm, 25 °C), in acetone, results in the formation of the 1-naphthoyl compound (**2b**).¹⁴ Heating or bubbling a slow stream of nitrogen through this solution of **2b** results in the deinsertion of carbon monoxide yielding **1b** quantitatively after several hours. Crystals of **2b**, suitable for X-ray structure analysis,¹⁵ were obtained by slow distillation of pentane into an acetone solution of **2b** under a CO atmosphere.

The molecular structure of the cation $[\text{Pd}(\text{1-naphthoyl})(\text{NN}'\text{N})]^+$ is shown in the figure.¹⁵ In this square planar palladium(II) complex the naphthoyl ligand is bonded by the carbonyl carbon atom in trans position to the pyridine nitrogen atom N(1). The nitrogen atoms of the CH_2NMe_2 groups, N(2) and N(3), are bonded mutually trans, so forming two $\text{PdNCCN}(1)$ five membered chelate rings. The Pd-N(1) bond length (2.042(4) Å) is very short in comparison with the Pd-N bond length of 2.131(4) Å found for the 2,2'-bipyridyl nitrogen atom trans to the methyl group in the cationic complex $[\text{PdMe}(2,2'\text{-bipyridyl})(\gamma\text{-picoline})]^+$.¹⁶ The short Pd-N(1) bond is accompanied by a small N(2)-Pd-N(3) angle (159.67(19)°) which is an indication of considerable steric strain. These structural features are due to the terdentate bonding mode as was also found for the related complexes $[\text{PdMe}(2,2':6,2'\text{-terpyridyl})]\text{Cl}\cdot 2\text{H}_2\text{O}$ ¹⁷ and $[\text{PdCl}(2,2':6,2'\text{-terpyridyl})]\text{Cl}\cdot 2\text{H}_2\text{O}$.¹⁸ In **2b**, the Pd-C distance (1.966(6) Å) is comparable to the Pd-C distances found in neutral complexes with a chloride, instead of a nitrogen atom, trans to an acyl group (1.97(2) Å⁷ and 1.960(10) Å⁹). This indicates that the Pd-C bond distance is little affected by the group trans to it.

The carbonyl group of the 1-naphthoyl ligand shows a normal Pd-C(13)-O angle (119.0(5)°) and must hence be η^1 -bonded to the palladium; for an η^2 -bonded carbonyl group one would expect the Pd-C(13)-O angle to be much

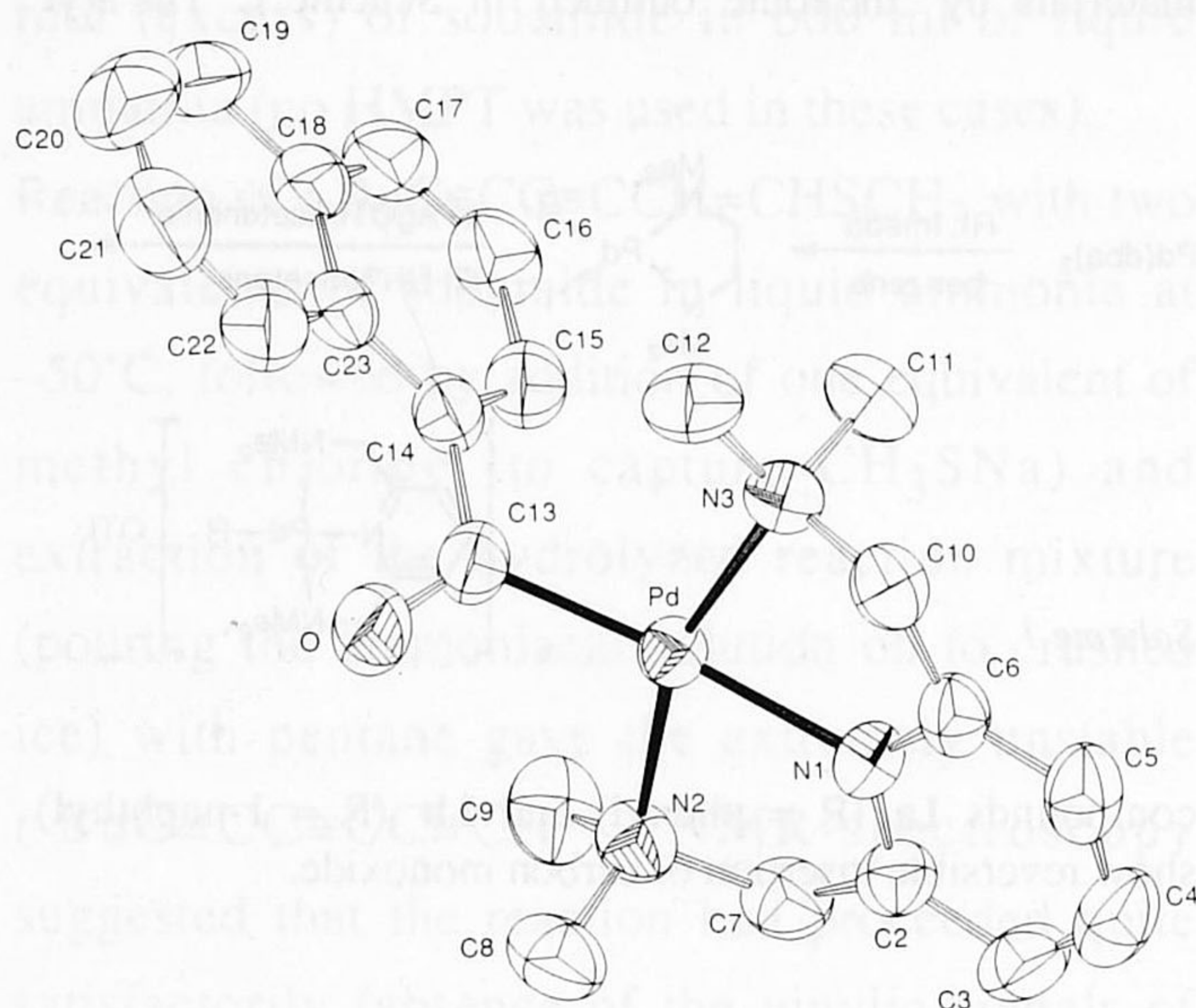
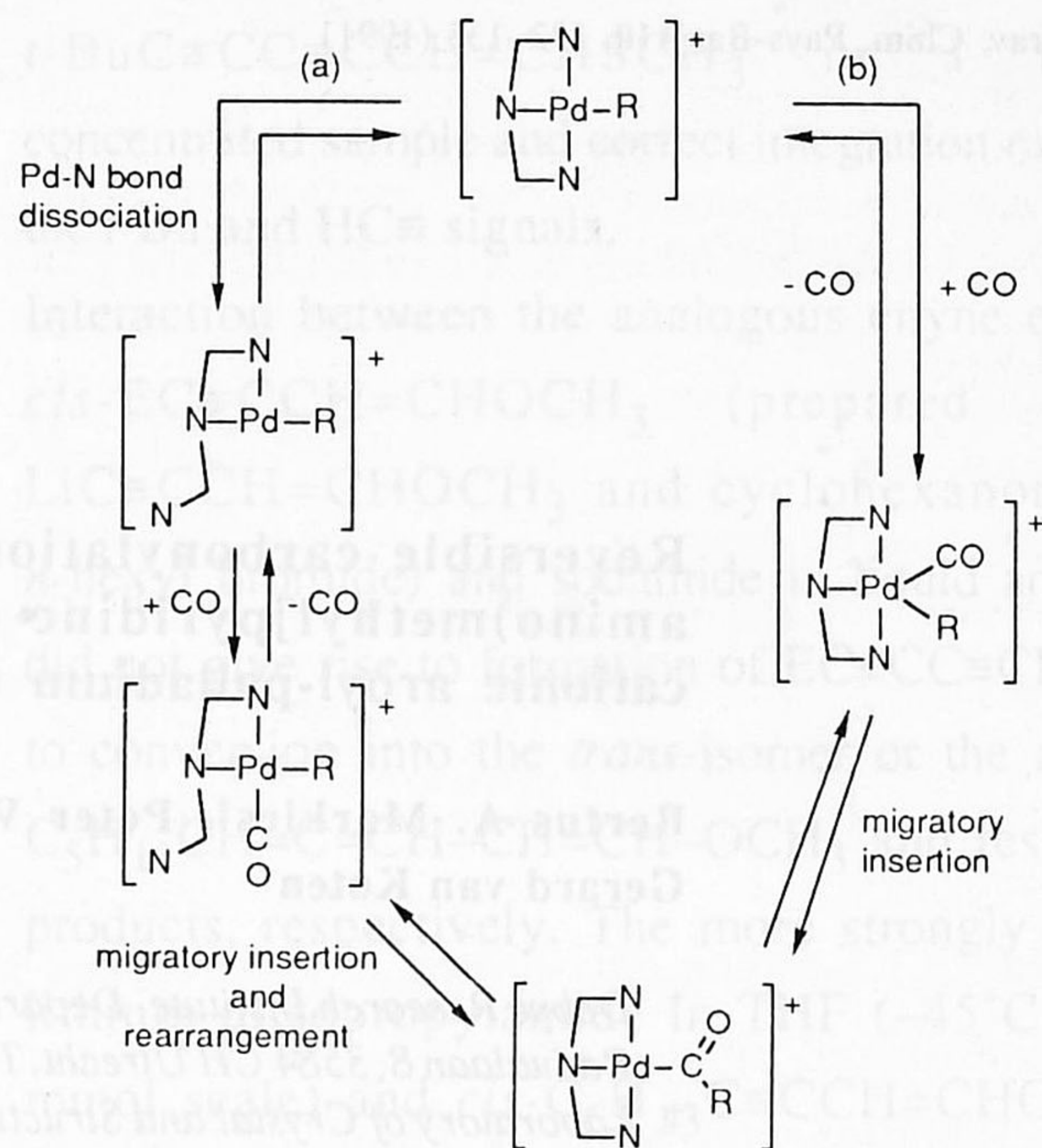


Fig. ORTEP drawing (50 % probability level) of compound **2b** with the adopted numbering scheme.



Scheme 2.

smaller. An example of such an η^2 -bonding mode was found in $\text{TiCl}(\text{COMe})\text{Cp}_2$, which shows an acute Ti-C-O angle of 79.7(6)°.¹⁹ The normal Pd-C(13)-O angle in **2b** also indicates that there is no repulsion between the palladium centre and the oxygen atom of the carbonyl group, as was found for *trans*- $\text{PdCl}(\text{C}(\text{O})\text{C}(\text{O})\text{OMe})\text{-}(\text{PPh}_3)_2$.⁷

The insertion of CO into the Pd-C bond of **1a** and **1b** is a moderately slow reaction which goes to completion within 30 min for **1a** and 3 h for **1b**. Particularly interesting is the reversibility of this process in solution since this is a relatively rarely observed phenomenon in palladium chemistry.^{20,21} The insertion and deinsertion processes can follow two possible routes (see Scheme 2). At first sight, the dissociative route (route *a*) seems to be the energetically more feasible since the dissociation of the Pd-N bond accomplishes two favorable things. Firstly, it allows lengthening of the Pd-N(1) bond, thus relieving the molecule of internal strain (*vide supra*). In the second place, it leaves an open site for CO coordination. However, the insertion and deinsertion rates of the 1-naphthyl species are both lower than those of the phenyl species, i.e. the insertion and deinsertion rates depend on the size of the organic group. Route *a* cannot account for this observation. We suggest therefore the reaction to follow the associative route (route *b*) and attribute these rate differences to the different steric crowding in the five coordinate intermediates. Furthermore, for initial coordination of CO at the palladium center in **1b**, one of the two potential coordination sites is blocked by the proton bound to C22 (see Figure). Secondary evidence for the associative route comes from the observation that crystallization of **2a** has so far failed, whereas this proceeds readily with **2b**. This can be explained by the bulk of the naphthyl ligand, in the five-coordinate intermediate, providing a kinetic barrier to the deinsertion process.

Acknowledgement. X-ray data were collected by A. J. M. Duisenberg. We thank Dr D. M. Grove for his valuable suggestions and the careful reading of this document. This work was supported in part (A. L. S.) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

References and Notes

- ¹ P. M. Maitlis, "The Organic Chemistry of Palladium", Academic Press, London (1971).
- ² P. A. Chaloner, "Handbook of Coordination Catalysis in Organic Chemistry", Butterworths, London (1986).
- ³ A. Yamamoto, "Organotransition Metal Chemistry", J. Wiley & Sons, New York (1986).
- ⁴ F. Calderazzo, *Angew. Chem. Int. Ed. Engl.* **16**, 299 (1977).
- ⁵ E. J. Kuhlmann and J. J. Alexander, *Coord. Chem. Rev.* **33**, 195 (1980).
- ⁶ G. K. Anderson and R. J. Cross, *Acc. Chem. Res.* **17**, 67 (1984).
- ⁷ J. Fayos, E. Dobrzynski, R. J. Angelici and J. Clardy, *J. Organomet. Chem.* **59**, C33 (1973).
- ⁸ R. Bardi, A. Del Pra, A. M. Piazzesi and L. Toniolo, *Inorg. Chim. Acta* **35**, L345 (1979).
- ⁹ R. Bardi, A. M. Piazzesi, G. Cavinato, P. Cavoli and L. Toniolo, *J. Organomet. Chem.* **224**, 407 (1982).
- ¹⁰ R. Bardi, A. M. Piazzesi, A. Del Pra, G. Cavinato and L. Toniolo, *Inorg. Chim. Acta.* **102**, 99 (1985).
- ¹¹ A. Sen, J.-T. Chen, W. M. Vetter and R. R. Whittle, *J. Am. Chem. Soc.* **109**, 148 (1987).
- ¹² B. A. Markies, P. Wijckens, J. Boersma, A. L. Spek and G. van Koten, to be published.
- ¹³ To a solution of Pd(dba)₂ (1.15 g, 2 mmol) in benzene (20 mL), under a nitrogen atmosphere, was added 1-iodonaphthalene (0.52 g, 2 mmol) and N,N,N',N'-tetramethylethylenediamine (0.33 mL, 2.2 mmol). The solution was heated at 50 °C until the colour changed from purple to dark green (2-5 min). After filtration of the solution through a sintered-glass filter, the filtrate was evaporated to dryness. The brown residue was washed with dry diethyl ether (4 x 60 mL) and was subsequently dissolved in acetonitrile (10 mL). To this solution AgOTf (0.51 g, 2 mmol) was added, whereupon a yellow solid and a brown solution formed. The solution was filtered and the residue washed with acetone. After removing the volatiles *in vacuo*, the resulting red oil was taken up in acetone (20 mL) and 2,6-bis[(dimethylamino)methyl]pyridine (0.45 g, 2.3 mmol) was added. The solution was stirred at 50 °C for 2 h after which the solvent was removed *in vacuo*. The residue was washed with acetone (3 x 50 mL) and the pure product obtained by trituration with pentane. Yield 0.69 g (60%) of **1b**. ¹H NMR (200 MHz, CD₃COCD₃): δ 2.63 (s, 6H, NMe₂); 2.77 (s, 6H, NMe₂); 4.64 (m, 4H, -CH₂-); 7.25 (dd, 1H, naphthyl); 7.41 (m, 1H, naphthyl); 7.53 (m, 2H, naphthyl); 7.68 (d, *J* = 7.9 Hz, 2H, 3,5-II(Py)); 7.77 (m, 2H, naphthyl); 8.17 (t, *J* = 7.9 Hz, 1H, 4-II(Py)); 9.29 (d, *J* = 8.3 Hz, 1H, naphthyl). ¹³C NMR (50 MHz, CD₃COCD₃): δ 52.73, 53.39 (NMe₂); 74.27 (-CH₂-); 121.85 (3,5-C(Py)); 124.25, 125.41, 125.71, 125.92, 129.24, 130.98, 132.63, 134.95, 139.39 (naphthyl); 141.56 (4-C(Py)); 156.92 (2,6-C(Py)); 161.89 (naphthyl).
- ¹⁴ A solution of **1b** (300 mg, 0.5 mmol) in acetone (15 mL) was treated with carbon monoxide (1 atm) for 3 h. After filtration the volatiles were evaporated *in vacuo*. The product was successfully crystallized from acetone/pentane in a carbon monoxide atmosphere. No yield was determined but ¹H NMR spectroscopy shows the reaction to be complete after 3 h. ¹H NMR (200 MHz, CD₃COCD₃): δ 2.75 (s, 12H, NMe₂); 4.52 (s, 4H, -CH₂-); ca. 7.8 (m, 9H, Py + naphthyl); 8.82 (d, *J* = 8.3 Hz, 1H, naphthyl). IR(KBr): ν_{CO} = 1615 cm⁻¹.
- ¹⁵ Crystal data for **2b**: C₂₃H₂₆F₃N₃O₄PdS: space group *P*₇; cell dimensions *a* = 8.742(1) Å, *b* = 12.303(1) Å, *c* = 13.563(1) Å, α = 116.33(1)°, β = 89.92(1)°, γ = 103.47(1)°; *Z* = 2; *V* = 1262.7(2) Å³; *d* = 1.588 g.cm⁻³. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer [MoKα, λ = 0.71073 Å, θ_{max} = 27.5°] for a needle shaped crystal glued on top of a glass fiber. A total of 6775 reflections were scanned, corrected for Lp and absorption (DIFABS²²) and merged into a unique set of 4201 reflections with *I* > 2.5σ(*I*). The structure was solved with direct methods (SHELXS86²³) and refined on *F* to *R* = 0.055 with SHELX76.²⁴ Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Center.
- ¹⁶ P. K. Byers, A. J. Canty, B. W. Skelton and A. H. White, *J. Organomet. Chem.* **336**, C55 (1987).
- ¹⁷ R. E. Rülke, I. M. Han, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, C. F. Roobeek, M. C. Zoutberg, Y. F. Wang and C. H. Stam, *Inorg. Chim. Acta* **169**, 5 (1990).
- ¹⁸ G. M. Intille, C. E. Pfluger and W. A. Baker Jr, *J. Cryst. Mol. Struct.* **3**, 47 (1973).
- ¹⁹ G. Fachinetti, C. Floriani and H. Stoeckli-Evans, *J. Chem. Soc. Dalton Trans.*, 2297 (1977).
- ²⁰ J. Dupont, M. Pfeiffer, J. C. Daran and Y. Jeannin, *Organometallics* **6**, 899 (1987).
- ²¹ M. A. Cinellu, S. Gladiali and G. Minghetti, *J. Organomet. Chem.* **363**, 401 (1989).
- ²² N. Walker and D. Stuart, *Acta Crystallogr., Sect. A.* **39**, 158 (1983).
- ²³ G. M. Sheldrick, SHELXS86, program for crystal structure determination; University of Göttingen, Göttingen, Federal Republic of Germany (1986).
- ²⁴ G. M. Sheldrick, SHELX76, crystal structure analysis package; University of Cambridge, Cambridge, England, 1976.