182. Investigations of Steric and Electronic Factors Influencing the Cyclopalladation of *meta*-Toluidine Analogues

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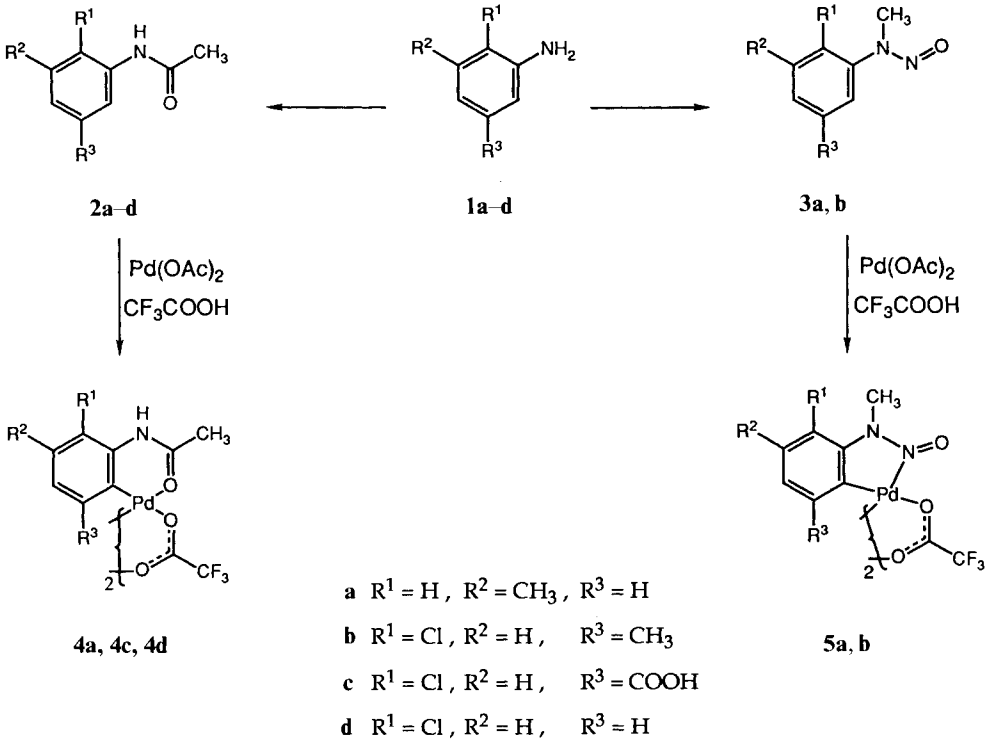
The cyclopalladation of two different types of aniline derivatives is described: the acetylated anilines *N*-(3-methylphenyl)acetamide (**2a**), 3-(acetylamino)-4-chlorobenzoic acid (**2c**), and *N*-(2-chlorophenyl)acetamide (**2d**) are cyclometalated easily with palladium(II) acetate and trifluoroacetic acid to yield the corresponding complexes **4a**, **4c**, and **4d**, respectively, whereas the acetylated *meta*-toluidine *N*-(2-chloro-5-methylphenyl)acetamide (**2b**) cannot be metalated at the only accessible site between the acetylamino and the methyl group. This aromatic C–H bond can be activated, however, with the second type of *meta*-toluidine derivatives: the 2-chloro-5,*N*-dimethyl-*N*-nitrosoaniline (**3b**) readily undergoes cyclopalladation to yield the corresponding Pd^{II} complex di-μ-trifluoroacetato-bis[3-chloro-6-methyl-2-(*N*-methyl-*N*-nitrosoamino)phenyl-C,*N*=O]dipalladium(II) (**5b**) containing a five-membered palladacycle with coordination of Pd^{II} at the nitroso N-atom, which is established by ^{15}N-NMR spectroscopy.

Introduction. – We attempt to activate the *ortho*-positions to the amino function of *meta*-toluidine (**1a**) in order to introduce sequentially *ortho*-substituents such as *e.g.* halogens into the aromatic moiety. C–H Bonds in suitable arenes are well-known for being able to be replaced quite easily by means of the cyclo*metal*ation reaction [1–3]. Cyclo*pallad*ation usually leads to stable complexes which can be cleaved subsequently with a great variety of reagents [4–7]. These reactions lead to novel functionalized arenes or aromatic heterocycles, which cannot be obtained by conventional methods or can be synthesized only with great difficulty in several reaction steps. Catalytic conversion of a suitable aromatic compound with regioselective *ortho*-halogenation was reported by *Fahey* [8] among others, which obviously must involve an intermediate cyclopalladation step. We reported on a ring closure reaction with alkylated arylazonaphthalenes catalyzed by Pd^{II} [9]. In this process, indazoles seem to be formed also *via* a cyclopalladated intermediate.

Results and Discussion. – To cyclopalladate a *meta*-toluidine species of structure **1** (*Scheme*), a donor substituent is needed to serve as a pre-coordination site for the metal-reagent complex. Furthermore, the resulting palladacycle should be a five- or six-membered ring [2]. For aromatic amines, the acetylation of the NH_2 group is a very convenient method of introducing a protecting group which can easily be removed after regioselective substitution steps to yield the target molecule [10–13]. The acetylamino substituent offers the palladium species an oxygen donor for pre-coordination and results in the formation of a six-membered ring upon cyclometalation.

The reaction conditions of the cyclopalladation had to be optimized. We applied a modified version of the cyclopalladation according to *Gontcharov et al.* [14] with the

Scheme



addition of excess CF_3COOH (TFA), which is thought to produce a more reactive (*i.e.* more electrophilic) palladium species like an ionic oligomeric trifluoroacetate complex with Pd^{II} [15]. The reaction conditions and yields of the cyclopalladations with the acetanilides **2a–d** are shown in the *Table*.

Table. *Cyclopalladation of Acetanilides* **2a–2d** *and of the* N-*Methyl*-N-*nitroso Derivatives* **3a** *and* **3b** *with* $Pd(OAc)_2$ *in Dioxane with Addition of TFA*

Starting material	Starting mat. [mM][a])	Equiv. Pd^{II}[b])	Equiv. TFA/Pd^{II}[c])	Temp. [°C]	Reaction time [h]	Yield [%][d])
2a	163	0.5	5	70	2.5	94
2b	84	0.5	20	50–70	2–20	no reaction
2c	95	0.5	23	70	8	80
2d	90	0.5	28	50	2	86
3a	125	0.5	20	65	8	69
3b	80	0.92	22	65	4	76

[a]) Concentration [mmol/l] of starting material in the reaction mixture.
[b]) Molar ratio of $Pd(OAc)_2$ to starting material.
[c]) Molar ratio of TFA to $Pd(OAc)_2$.
[d]) Yield relative to Pd^{II}.

The reaction of the 3-methylacetanilide (**2a**) with $Pd(OAc)_2$ smoothly yields the corresponding Pd^{II} complex **4a**, whereas the acetanilide **2b** resists cyclometalation to the complex **4b** under the same conditions. This unreactivity of **2b** towards cyclopalladation might be due to the steric hindrance by the Me group in conjunction with the deactivation of the aromatic ring by the Cl substituent. Furthermore, the formation of a six-membered chelate upon cyclopalladation involving an oxygen donor seems to be unfavorable in this case. Nevertheless, the cyclopalladation of the derivative **2c** with a COOH instead of a Me substituent easily yields the complex **4c**, which could be explained by the neighboring-group effect exerted by the COOH donor. Electronic deactivation by the Cl substituent does not seem to be important, as the cyclopalladation of the 2-chloroacetanilide (**2d**) without a *meta*-Me group leads to the corresponding complex **4d** in good yield.

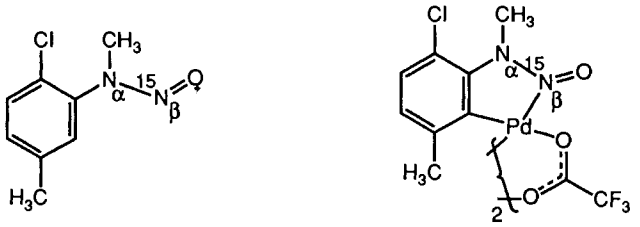
The structures of the resulting Pd^{II} complexes **4a**, **4c**, and **4d** have been assigned with the aid of ^{1}H-NMR spectroscopy. The spectrum of **4a** in (D_6)acetone shows a *singlet* and two *doublets* of an *AB*-coupling system. This is consistent with palladation at the C-atom *para* to the Me substituent. No signals were found of an isomeric complex in which the Pd–C bond is *ortho* to the Me group. The ^{1}H-NMR spectrum for complex **4c** in (D_6)DMSO reveals only one *AB*-coupling system with two *doublets* for the two aromatic protons, which confirms the proposed cyclopalladated structure for **4c**. Besides resonances for the acetyl Me group and the NH proton, no other signals could be detected; in particular the signal for the COOH proton seems to be absent. This would suggest that the COOH group is deprotonated and is interacting ionically with the Pd centre. A corroboration of this hypothesis will be available after an X-ray structure assignment and will be published elsewhere.

The lack of reactivity of the acetanilide **4b** towards cyclopalladation obviously results from steric hindrance by the Me substituent together with unfavorable pre-coordination equilibria due to the oxygen donor and with the potential formation of a thermodynamically less favorable six-membered palladacycle. Therefore, another donating substituent was devised [16] [17] and the corresponding *N*-methyl-*N*-nitroso-toluidines **3a** and **3b** were synthesized (*Scheme*). Reaction of these nitroso compounds under similar conditions as the acetanilides **2a–d** led to the corresponding cyclopalladated complexes **5a** and **5b** in satisfactory yields (*Table*).

These results prove that the steric hindrance by the Me substituent does not prevent cyclopalladation, if instead of the acetanilide **2b** the corresponding *N*-nitroso analogue **3b** is treated with $Pd(OAc)_2$ and TFA: with this N-donor ligand, cyclopalladation readily occurs to yield complex **5b** containing a five-membered palladacycle.

The ^{1}H-NMR spectrum of the complex **5a** is in agreement with the postulated structure: one *singlet* for the proton *ortho* to the Me and the nitroso-amino substituents and two *AB*-coupling *doublets* for the other two aromatic protons confirm that cyclopalladation occurred *para* to the Me group.

The structure determination for the complex **5b** by ^{1}H-NMR leads to the conclusion that the metalation at the only C–H bond accessible for the Pd^{II} centre did take place: the original *singlet* in the nitroso compound **3b** for the proton between the Me and the nitroso-amino substituents disappeared, whereas an *AB*-coupling pattern with two *doublets* for the remaining two aromatic protons proves metalation at the envisaged site of the aromatic ring. The assumption that a five-membered ring with coordination of the Pd centre at the N-donor was verified by ^{15}N-NMR techniques: the ^{15}N-labelled analogue of



3b ($^{15}N_{\beta}$=O) **5b** ($^{15}N_{\beta}$=O)

$\delta(^{15}N_{\beta})$/[ppm]	553.2	404.3

Figure. *^{15}N-NMR Data for* **3b**(^{15}N=O) *and* **5b**(^{15}N=O) ((D$_6$)acetone, 40 MHz; δ relative to NH_3(l) as internal standard)

the *N*-nitroso compound **3b** was cyclopalladated to the corresponding labelled complex **5b**(^{15}N=O). The observed difference between the ^{15}N resonance of the ^{15}N-centre of the ligand **3b** and that one of the complex **5b** of *ca.* 150 ppm towards higher field (*Fig.*) is in full agreement with data obtained by *Pregosin* and coworkers [17] for similar complexes with coordination of Pd^{II} at a ^{15}N-labelled N-donor. These results strongly suggest that the palladacycle is closed *via* coordination at the N-atom of the N=O group to the proposed five-membered ring structure **5b**.

Conclusions. – To activate both *ortho*-positions in *meta*-toluidines, it was necessary to synthesize the *N*-methyl-*N*-nitroso derivatives of general structure **3**: only with the corresponding compound **3b** did the position between the amino function and the Me group become accessible for cyclometalation by Pd^{II}. With the acetylated *meta*-toluidines of type **2**, however, such a C–H bond activation was not possible, except for the carboxylated analogue **2c**, where the coordinating support of the COOH function seemed to have enabled the cyclopalladation at the sterically demanding C-centre. An X-ray structure determination for the resulting complex **4c** will be carried out in order to elucidate the coordinating and topological arrangement around the Pd^{II} centre. Similar structure evaluations for the novel complex **5b** obtained by cyclopalladation of compound **3b** should corroborate the strong evidence for the coordination of Pd^{II} at the nitroso N-atom as derived from preliminary ^{15}N-NMR investigations with the corresponding labelled complex **5b**($^{15}N_{\beta}$=O).

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Experimental Part

General. All commercially available chemicals employed were reagent grade and used without further purification, unless otherwise stated. $Pd(OAc)_2$ was purchased from *Johnson, Matthey, Brandenberger AG*. Reactions with organometallic reagents were carried out in dioxane (*Fluka, puriss.*) which had been dried over KOH before use. M.p.: *Büchi-SMP-20* capillary apparatus; uncorrected. IR Spectra: *Perkin-Elmer 783* infrared spectrometer; region 4000–400 cm^{-1}; KBr matrix, unless otherwise stated. ^1H- and ^{13}C-NMR Spectra: *Bruker AM300 WB* or *Bruker AC200 P* spectrometer; δ in ppm with TMS as internal standard, coupling constants J in Hz. ^{15}N-NMR Spectra: *Bruker AMX400 WB* spectrometer, δ in ppm relative to $NH_3(l)$ as internal standard. ^{19}F-NMR Spectra: *Bruker AC200 P* spectrometer, δ in ppm relative to $CFCl_3$ as external standard. MS: *Hitachi-Perkin-Elmer RMU-6M*, electron impact EI; FAB spectra: *ZAB2-SEQ* spectrometer; peaks in % rel. to intensity of base peak (= 100%) *vs.* *m/z*. Elemental analyses were performed at the Laboratory of Organic Chemistry; Pd contents were determined by AAS at the Inorganic Chemistry Laboratory (Prof. *B. Magyar*).

Acetanilides **2a–d**. Syntheses according to standard methods for acetylations [18] with Ac_2O in dioxane in the presence of pyridine. Extraction of a soln. of the crude product in Et_2O or in CH_2Cl_2 with 10% H_2SO_4 (aq.) and recrystallization from toluene/hexane, except for **2c**, which precipitated directly from dioxane and was only washed with CH_2Cl_2.

N-*(3-Methylphenyl)acetamide* (**2a**). M.p. 66°. IR: 1665*vs* (C=O). ^1H-NMR ((D$_6$)acetone, 300 MHz): 2.06 (*s*, $COCH_3$); 2.27 (*s*, CH_3); 6.85 (*d*, *J* = 7.5, H–C(4)); 7.14 (*dd*, *J* = 7.7, H–C(5)); 7.43 (*d*, *J* = 7.7, H–C(6)); 7.47 (*s*, H–C(2)); 9.04 (br. *s*, NH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 21.4 ($COCH_3$); 24.5 (CH_3); 117.1 (C(6)); 120.7 (C(2)); 125.1 (C(4)); 128.7 (C(5)); 137.9 (C(3)); 138.8 (C(1)); 168.6 (C=O). MS (I > 5%): 150 (13), 149 (51, M^+), 108 (9), 107 (100), 106 (39), 77 (7), 43 (15).

N-*(2-Chloro-5-methylphenyl)acetamide* (**2b**). M.p. 98°. IR: 1665*vs* (C=O). ^1H-NMR ((D$_6$)acetone, 300 MHz): 2.18 (*s*, $COCH_3$); 2.30 (*s*, CH_3); 6.93 (*dd*, *J* = 8.2, 1.6, H–C(4)); 7.28 (*d*, *J* = 8.2, H–C(3)); 8.00 (*d*, *J* = 1.6, H–C(6)); 8.54 (br. *s*, NH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 21.4 ($COCH_3$); 25.0 (CH_3); 119.6 (C(2)); 122.2 (C(6)); 125.5 (C(4)); 128.6 (C(3)); 134.2 (C(5)); 138.0 (C(1)); 168.3 (C=O). MS (I > 5%): 186 (26), 184 (11), 183 (65, M^+), 149 (21), 148 (87), 143 (74), 142 (39), 141 (100), 140 (35), 107 (14), 106 (82), 104 (17), 79 (13), 78 (21), 77 (68), 63 (14), 52 (14), 51 (32), 50 (11), 43 (79), 39 (16), 28 (21), 18 (15), 15 (12).

3-(Acetylamino)-4-chlorobenzoic Acid (**2c**). M.p. 133°. IR: 1680*vs* (C=O(OH)), 1670*vs* (C=O). ^1H-NMR ((D$_6$)DMSO, 300 MHz): 2.12 (*s*, $COCH_3$); 7.61 (*d*, *J* = 7.5, H–C(5)); 7.71 (*dd*, *J* = 7.5, 2.0, H–C(6)); 8.33 (*d*, *J* = 2.0, H–C(2)); 9.63 (br. *s*, NH); 13.07 (br. *s*, COOH). ^{13}C-NMR ((D$_6$)DMSO, 75 MHz): 23.3 ($COCH_3$); 123.8 (C(2)); 126.4 (C(5), (H–C from DEPT)); 129.6 (C(6), (H–C from DEPT)); 130.0 (C(1)); 130.5 (C(4)); 135.2 (C(3)); 166.3 (COOH); 168.8 (C=O).

N-*(2-Chlorophenyl)acetamide* (**2d**). M.p. 85°. IR: 1660*s* (C=O). ^1H-NMR ((D$_6$)acetone, 300 MHz): 2.19 (*s*, $COCH_3$); 7.14 (*ddd*, *J* = 9.5, 1.6, H–C(5)); 7.26 (*ddd*, *J* = 9.2, 1.6, H–C(4)); 7.43 (*dd*, *J* = 9, 0.9, H–C(3)); 8.15 (*dd*, *J* = 9, 0.9, H–C(6)); 8.6 (br. *s*, NH). ^{13}C-NMR ($CDCl_3$, 75 MHz): 24.8 ($COCH_3$); 121.6 (C(6)); 124.6 (C(4)); 127.7 (C(2)); 127.7 (C(5)); 128.9 (C(3)); 134.6 (C(1)); 168.2 (C=O). MS (I > 5%): 171 (5), 169 (14, M^+), 134 (26), 129 (30), 128 (7), 127 (100), 99 (6), 92 (8), 91 (5), 65 (7), 64 (5), 63 (7), 43 (30), 32 (8), 28 (37), 18 (86), 17 (20), 15 (15).

N-*Methyl*-N-*nitrosoanilines* **3a** *and* **3b**. Obtained from a three-step synthesis according to [19] [20] from the anilines *via* the corresponding *N*-methylformanilide and the *N*-methylaniline.

*3,*N-*Dimethyl*-N-*nitrosoaniline* (**3a**). *m*-Toluidine (**1a**; 10 ml, 92 mmol), trimethyl orthoformate (15 ml, 138 mmol), and conc. aq. H_2SO_4 (0.2 ml, 3.3 mmol) were mixed in this order. After 5 min at 80°, the turpid soln. began to boil with evolution of MeOH, which was distilled off *via* a *Vigreux* column by heating up to 120° during 2 h. For the completion of the reaction, the temp. was kept at 180° during 30 min. The 3,*N*-dimethylformanilide was used as starting material for the next step without isolation: 33 ml of H_2O and 12 ml of conc. HCl were added and the yellow suspension was boiled at 100° during 2.5 h. After cooling down, NaOH (s; 11.4 g, 0.3 mmol) was added to the orange soln. The soln. of pH 8 was extracted twice with 50 ml of Et_2O and the org. phases combined, dried ($MgSO_4$) and the solvent distilled off. The resulting *N*-methyl-*m*-toluidine was used directly in the following reaction step: 35 g of ice and 13 ml of conc. HCl were added, and the temp. was kept carefully at 0°. Then, a soln. of $NaNO_2$ (6.35 g, 91 mmol) in 20 ml of H_2O was added slowly with vigorous stirring and keeping the temp. of the soln. below 5°. After a reaction time of 2.5 h, the bi-phasic mixture was extracted twice with 100 ml of Et_2O. The org. phase was dried ($MgSO_4$) and the solvent evaporated to yield an orange-red oil, which was distilled by fractionation (150°/0.1 Torr): **3a** (6.69 g, 48.5%). ^1H-NMR ((D$_6$)acetone, 300 MHz): 2.42 (*s*, CH_3); 3.44 (*s*, $N(NO)CH_3$); 7.22 (*m*, H–C(6)); 7.41 (*d*, *J* = 8, H–C(5)); 7.42 (*d*, *J* = 2, H–C(4)); 7.47 (*m*, H–C(2)). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 21.5 (CH_3); 31.6 ($N(NO)CH_3$); 117.3 (C(6)); 120.8 (C(4)); 128.7 (C(5)); 130.1 (C(2)); 140.3 (C(3)); 143.5 (C(1)).

*2-Chloro-5,*N*-dimethyl-*N*-nitrosoaniline* (**3b**). Obtained by the same method as **3a**, starting from *2-chloro-5-methylaniline* (**1b**): orange-red oil of **3b** (46%, over all three steps). ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 2.42 (*s*, CH$_3$); 3.36 (*s*, N(NO)CH$_3$); 7.38 (*d*, *J* = 8, H–C(4)); 7.40 (*s*, H–C(6)); 7.54 (*d*, *J* = 8, H–C(3)). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 20.7 (CH$_3$); 35.1 (N(NO)CH$_3$); 127.7, 129.7, 131.1, 132.2, 139.6, 162.9 (C(arom.)).

Cyclopalladation of the Acetanilides **2a**, **2c**, *and* **2d**: *Pd^{II} Complexes* **4a**, **4c**, *and* **4d**. Carried out by mixing the acetanilide, Pd(OAc)$_2$, and CF$_3$COOH (TFA) in dioxane; for relative molar amounts of Pd^{II} and TFA, reaction temp., reaction time, and yields under the optimal reaction conditions, *cf.* the *Table*.

*Di-μ-trifluoroacetato-bis[2-(acetylamino)-4-methylphenyl-*C,O*]dipalladium(II)* (**4a**). M.p. 112° (dec.). IR: 3330*m*, 3180*w*, 2920*w*, 2860*w*, 1665*vs*, 1630*s*, 1595*s*, 1535*m*, 1470*s*, 1435*m*, 1375*m*, 1323*w*, 1225*w*, 1200*vs*, 1150*s*, 1045*m*, 1035*m*, 855*m*, 840*w*, 800*s*, 790*w*, 775*w*, 730*s*, 720*m*, 700*w*, 660*m*, 611*m*, 515*w*, 460*m*, 440*w*, 390*w*. ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 1.47 (*s*, COCH$_3$); 2.24 (*s*, CH$_3$); 6.70 (*s*, H–C(3)); 6.72 (*d*, *J* = 7.8, H–C(6)); 6.90 (*d*, *J* = 7.8, H–C(5)); 10.37 (br. *s*, NH). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 20.2 (CO*C*H$_3$); 20.4 (CH$_3$); 112.7, 116.1 (*q*, CF$_3$); 117.2, 124.8, 131.8, 133.4, 135.7 (C(arom.)); 167.8 (C=O). FAB-MS (I > 5%): 738 (5), 736 (7), 735 (5, M^+), 734 (6), 733 (5), 732 (5), 627 (7), 625 (14), 624 (10), 623 (19), 622 (15), 621 (16), 620 (15), 619 (13), 618 (7), 405 (5), 403 (7), 401 (6), 364 (5), 362 (7), 361 (6), 360 (8), 359 (7), 358 (9), 357 (6), 258 (8), 257 (6), 256 (16), 255 (7), 254 (20), 253 (17), 252 (13), 251 (5), 194 (5), 154 (6), 149 (19), 148 (100), 147 (8), 146 (5), 136 (7), 120 (5), 108 (5), 107 (8), 106 (7), 105 (5), 91 (6), 89 (5), 77 (8).

*Di-μ-trifluoroacetato-bis[2-(acetylamino)-3-chloro-6-carboxyphenyl-*C,O*]dipalladium(II)* (**4c**). Insoluble in Et$_2$O, acetone, CHCl$_3$, CH$_3$CN, CCl$_4$, CH$_3$OH, soluble in DMSO and DMF. M.p. 260° (dec.). IR: 3400*s*, 3380*s*, 3100*m*, 2925*w*, 2830*w*, 1680*vs*, 1605*vs*, 1530*vs*, 1430*m*, 1400*vs*, 1384*m*, 1320*vs*, 1200*vs*, 1145*s*, 1090*m*, 1035*w*, 870*w*, 830*m*, 800*m*, 770*m*, 720*m*, 710*m*, 650*m*, 600*m*, 580*m*, 460*m*. ^{1}H-NMR ((D$_6$)DMSO, 300 MHz): 2.36 (*s*, COCH$_3$); 6.93 (*d*, *J* = 7.9, H–C(4)); 7.23 (*d*, *J* = 7.9, H–C(5)); 10.50 (br. *s*, NH). ^{13}C-NMR ((D$_6$)DMSO, 125 MHz): 22.6 (CO*C*H$_3$); 125.2 (C(4)/C(5), (H–C from DEPT)); 125.7 (C(5)/C(4), (H–C from DEPT)); 120.7, 127.3, 128.1 (C(2), C(3), C(6)); 140.2 (C(1)–Pd); ≈ 161 (br., CF$_3$*C*OO$^-$); 169.3 (*C*OCH$_3$); 176.5 (COOH). ^{19}F-NMR ((D$_6$)DMSO, 300 MHz): –73.11 (CF$_3$). Anal. calc. for C$_{11}$H$_7$ClF$_3$NO$_5$Pd (432.0): C 30.58, H 1.63, N 3.24, Pd 24.63; found: C 32.37, H 2.81, N 2.61, Pd 24.65 ± 0.25.

*Di-μ-trifluoroacetato-bis[2-(acetylamino)-3-chlorophenyl-*C,O*]dipalladium(II)* (**4d**). M.p. 208° (dec.). IR: 3380*s*, 3070*w*, 1655*s*, 1625*m*, 1575*m*, 1560*w*, 1530*s*, 1500*w*, 1435*s*, 1410*w*, 1375*w*, 1320*w*, 1200*s*, 1145*s*, 1070*m*, 1035*w*, 850*m*, 785*m*, 760*m*, 745*m*, 730*m*, 710*m*, 690*w*, 650*m*, 605*w*, 595*w*, 520*w*, 470*w*, 440*w*. ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 1.84 (*s*, COCH$_3$); 6.90 (*m*, H–C(5), H–C(4)); 7.29 (*d*, *J* = 6.7, H–C(6)); 9.77 (br. *s*, NH). ^{13}C-NMR (CDCl$_3$, 75 MHz): 21.0 (CO*C*H$_3$); 119.2 (*q*, CF$_3$); 117.6, 122.2, 127.4, 129.1, 130.2 (C(2), C(3), C(4), C(5), C(6)); 152.5 (C(1)–Pd); 166.2 (CF$_3$*C*OO$^-$); 170.1 (*C*OCH$_3$). ^{19}F-NMR ((D$_6$)acetone, 300 MHz): –74.38 (CF$_3$). FAB-MS (I ≥ 9%): 776 (5, M^+), 665 (10), 663 (11), 662 (9), 661 (9), 429 (9), 427 (9), 413 (9), 411 (9), 307 (28), 289 (16), 278 (12), 277 (29), 274 (20), 273 (18), 272 (10), 242 (10), 240 (11), 238 (11), 237 (10), 170 (16), 168 (34), 166 (9), 165 (9), 156 (10), 155 (39), 154 (100), 153 (12), 152 (16), 139 (23), 138 (46), 137 (72), 136 (81), 135 (14), 134 (15), 124 (16), 123 (11), 122 (9), 121 (12), 120 (19), 119 (9), 108 (14), 107 (34), 106 (13), 105 (15), 95 (9), 91 (20), 90 (23), 89 (33), 79 (11), 78 (17), 77 (32), 64 (14).

*Di-μ-trifluoroacetato-bis[4-methyl-2-(*N*-methyl-*N*-nitrosoamino)phenyl-*C,*N*=O*]dipalladium(II)* (**5a**). A mixture of **3a** (0.062 g, 0.413 mmol), Pd(OAc)$_2$ (0.046 g, 0.206 mmol), TFA (0.3 ml, 4.0 mmol), and 3 ml dioxane was stirred for 8 h at 65°. The orange precipitate was filtered off and dried *in vacuo*: **5a** (0.052 g, 69%). M.p. 272° (dec.). IR (RbI): 3420*m*, 3020*w*, 2920*w*, 1690*vs*, 1670*vs*, 1490*vs*, 1455*s*, 1425*s*, 1410*s*, 1375*w*, 1315*vs*, 1295*vs*, 1275*m*, 1245*s*, 1200*vs*, 1125*vs*, 1015*m*, 985*m*, 830*vs*, 800*vs*, 720*vs*, 685*m*, 555*m*, 510*m*, 430*m*, 365*m*, 260*m*. ^{1}H-NMR (CD$_2$Cl$_2$, 300 MHz): 2.35 (*s*, CH$_3$); 2.81 (*s*, N(NO)CH$_3$); 6.48 (*s*, H–C(3)); 6.82 (*d*, *J* = 8.0, H–C(6)); 6.90 (*d*, *J* = 8.0, H–C(5)). ^{19}F-NMR (CD$_2$Cl$_2$, 200 MHz): –74.95 (CF$_3$). Anal. calc. for C$_{10}$H$_9$F$_3$N$_2$O$_3$Pd (368.5): C 32.59, H 2.46, N 7.60; found: C 33.11, H 2.96, N 7.28.

*Di-μ-trifluoroacetato-bis[3-chloro-6-methyl-2-(*N*-methyl-*N*-nitrosoamino)phenyl-*C,*N*=O*]dipalladium(II)* (**5b**). A mixture of **3b** (0.050 g, 0.272 mmol), Pd(OAc)$_2$ (0.056 g, 0.25 mmol), TFA (0.4 ml, 5.4 mmol), and 3 ml dioxane was stirred for 4 h at 65°. The red precipitate was filtered off and dried *in vacuo*: **5b** (0.076 g, 76%). M.p. 210° (dec.). IR: 3420*w*, 2920*w*, 1655*vs*, 1570*w*, 1540*w*, 1510*s*, 1450*s*, 1380*w*, 1270*m*, 1200*vs*, 1150*s*, 1060*w*, 1035*m*, 855*m*, 825*w*, 805*m*, 780*w*, 730*s*, 675*m*, 540*w*, 520*w*, 420*w*. ^{1}H-NMR ((D$_6$)acetone, 300 MHz): 2.29 (*s*, CH$_3$); 3.48 (*s*, N(NO)CH$_3$); 6.86 (*d*, *J* = 8.0, H–C(4)); 7.23 (*d*, *J* = 8.0, H–C(5)). ^{13}C-NMR ((D$_6$)DMSO, 125 MHz): 23.5 (CH$_3$); 36.2 (N(NO)CH$_3$); 125.1, 126.8, 129.9, 140.8, 140.8 (C(2), C(3), C(4), C(5), C(6)); 142.7 (C(1)–Pd); 159.0 (*q*, *C*F$_3$COO$^-$). ^{19}F-NMR ((D$_6$)acetone, 300 MHz): –74.42 (CF$_3$). Anal. calc. for C$_{10}$H$_8$ClF$_3$N$_2$O$_3$Pd (403.0): C 29.80, H 2.00, N 6.95, O 11.91, Pd 26.40; found: C 29.89, H 2.02, N 6.78, O 12.01, Pd 24.54 ± 0.25.

^{15}N-Labelled Analogues **3b**(^{15}N=O) *and* **5b**(^{15}N=O). Synthesized in analogy to the syntheses of the unlabelled compounds **3b** and **5b**, except for the use of $Na^{15}NO_2$ (CIL, 99% ^{15}N) in the third step of the synthesis of **3b**.

3b(^{15}N=O): ^{15}N-NMR ((D_6)acetone, 40 MHz): 553.2 (*s*).

5b(^{15}N=O): ^{15}N-NMR ((D_6)acetone, 40 MHz): 404.3 (*s*).

REFERENCES

[1] M. I. Bruce, *Angew. Chem.* **1977,** *89,* 75.
[2] I. Omae, *Chem. Rev.* **1979,** *79,* 287.
[3] J. Dehand, M. Pfeffer, *Coord. Chem. Rev.* **1976,** *18,* 327.
[4] R. F. Heck, 'Palladium Reagents in Organic Synthesis', Academic Press, London, 1985.
[5] A. J. Klaus, P. Rys, in 'Chemistry of Functional Dyes', Eds. Z. Yoshida and T. Kitao, Mita-Press, Tokyo, 1989, pp. 123–138.
[6] A. D. Ryabov, *Synthesis* **1985,** 233.
[7] V. V. Dunina, O. A. Zelevskaya, V. M. Potapov, *Russian Chem. Rev.* **1988,** *57,* 250.
[8] D. R. Fahey, *J. Organomet. Chem.* **1971,** *27,* 283.
[9] M. Hugentobler, A. J. Klaus, P. Ruppen, P. Rys, *Helv. Chim. Acta* **1984,** *67,* 113.
[10] N. D. Cameron, M. Kilner, *J. Chem. Soc., Chem. Commun.* **1975,** 687.
[11] H. Horino, N. Inoue, *J. Org. Chem.* **1981,** *46,* 4416.
[12] H. Horino, N. Inoue, *Tetrahedron Lett.* **1979,** *26,* 2403.
[13] S. J. Tremont, H. U. Rahman, *J. Am. Chem. Soc.* **1984,** *106,* 5759.
[14] V. S. Gontcharov, V. S. Raida, E. E. Sirotkina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1986,** *3,* 77.
[15] R. N. Pandey, P. M. Henry, *Can. J. Chem.* **1974,** *52,* 1241.
[16] A. G. Constable, W. S. McDonald, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1980,** 2282.
[17] A. Albinati, S. Affolter, P. S. Pregosin, *J. Organomet. Chem.* **1990,** *395,* 231.
[18] 'Organikum', VEB Deutscher Verlag der Wissenschaften, Berlin, 1984, p. 512.
[19] R. M. Roberts, P. J. Vogt, *Org. Synth. Coll. Vol. IV* **1963,** 420.
[20] W. W. Hartmann, C. J. Roll, *Org. Synth.* **1933,** *13,* 82.