Organometallics **1992**, *11*, 3512–3517

Articles

Synthesis and Properties of *o*-Formylaryl Complexes of Palladium(II). Examples of Organometallic Reactions of Water-Soluble Arylpalladium(II) Complexes. Unusual Palladium-Assisted Rearrangement of $HC(O)C_6H_2(OMe)_3$-3,4,5 to $HC(O)C_6H_2(OMe)_3$-2,3,4. X-ray Structure of $[Pd\{C_6H(CHO)\text{-}6\text{-}(OMe)_3\text{-}2,3,4\}Cl(bpy)]$

José Vicente and José-Antonio Abad*

Grupo de Química Organometálica, Departamento de Química Inorgánica,
Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

Peter G. Jones*

Institut für Anorganische und Analytische Chemie der Technischen Universität,
Hagenring 30, 3300 Braunschweig, Germany

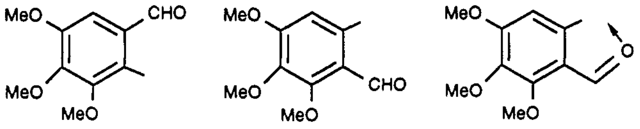
Received April 17, 1992

$[HgR_2]$ [R = $C_6H(CHO)$-6-$(OMe)_3$-2,3,4] reacts with $Q_2[Pd_2Cl_6]$ [Q = $(PhCH_2)Ph_3P$] to give $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ (**1**) and with $K_2[PdCl_4]$ in water/acetone solutions to give, after acetone and [HgRCl] are removed, an aqueous solution to which addition of dichloromethane solutions of 2,2′-bipyridine or 1,10-phenanthroline leads to [PdRCl(bpy)] (**2**) or [PdRCl(phen)] (**3**), respectively. Dichloromethane extracts from the above aqueous solutions the cyclometalated complex $[Pd_2(\eta^2\text{-}R')_2(\mu\text{-}Cl)_2]$ (**4**) which contains the rearranged aryl ligand R′ = $C_6H(CHO)$-2-$(OMe)_3$-3,4,5. **4** can also be obtained by reacting $[HgR_2]$ with $[PdCl_2(PhCN)_2]$. **4** reacts with 2,2′-bipyridine or 1,10-phenanthroline yielding [PdR′Cl(bpy)] (**2′**) or [PdR′Cl(phen)] (**3′**), respectively. Complexes **2**, **2′**, and **3** react with the appropriate potassium or silver salts and ligands to give $[PdR(bpy)(PPh_3)]CF_3SO_3$ (**5**), $[PdR'(bpy)(PPh_3)]CF_3SO_3$ (**5′**), $[PdR(bpy)(MeCN)]ClO_4$ (**6**), and $[PdR(phen)(MeCN)]ClO_4$ (**7**), respectively. Complexes **2′** and **3′** react with $AgClO_4$ to give the cyclometalated complexes $[Pd(\eta^2\text{-}R')(bpy)]ClO_4$ (**8**) and $[Pd(\eta^2\text{-}R')(phen)]ClO_4$ (**9**), respectively. The solid-state structure of **2** was determined by an X-ray diffraction study at −95 °C [crystals are orthorhombic, space group *Pbca*, with $Z = 8$, $a = 14.619$ (4) Å, $b = 16.185$ (5) Å, $c = 16.793$ (5) Å] which shows a distorted square-planar geometry around the palladium atom. The Pd–N bond distances show a clear difference in the trans influences of the aryl [Pd–N(1), 2.107 (3) Å] and chloro ligands [Pd–N(2), 2.039 (3) Å].

Introduction

Metal complexes bearing arylic groups containing reactive substituents (e.g. NO_2, NH_2) are not easily accessible by the traditional transmetalation reactions that use organolithium or Grignard reagents. We are currently interested in the preparation of these functionalized aryl complexes using organomercurials as transmetalating agents.[1] As far as we are aware, the only 2-formylaryl complexes reported are some mercury derivatives containing the aryl group $C_6H(CHO)$-6-$(OMe)_3$-2,3,4.[2] These compounds are, therefore, ideal starting materials for illustrating the synthesis of new types of complexes of other metals not accessible through the "standard" methods. In addition, the electron releasing methoxyl groups could confer special properties to the formyl group, for example, facilitating its coordination to metallic centers to give cyclometalated species. Finally, this aryl moiety is present in organic molecules of pharmaceutical interest, for example the antileukemic lactones steganacin and steganangin,[3] the antibacterial agent trimethoprim,[4] or the cytotoxic colchicine,[5] and we plan to use these aryl complexes in organic synthesis. Our results on the synthesis of organopalladium complexes bearing this group, as well as their involvement in an unusual rearrangement of the aryl ring, are the subject of this paper. Some of these results have been recently communicated.[6]

Chart I



R R′ η^2-R′

---

(1) Vicente, J.; Abad, J. A.; Lahoz, F. J.; Plou, F. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1459 and references cited therein.

(2) Sharp, T. M. *J. Chem. Soc.* **1937**, 852.

(3) Ziegler, F. E.; Chliwner, I.; Fowler, K. W.; Kanfer, S. J.; Kuo, S. J.; Sinha, N. D. *J. Am. Chem. Soc.* **1980**, *102*, 790. Tomioka, K.; Ishiguro, T.; Mizuguchi, H.; Komeshima, N.; Koga, K.; Tsukagoshi, S.; Tsuruo, T.; Tashiro, T.; Tanida, S.; Kishi, T. *J. Med. Chem.* **1991**, *34*, 54, and references cited therein.

(4) Chan, J. H.; Roth, B. *J. Med. Chem.*, **1991**, *34*, 550, and references cited therein.

(5) Ringel, I.; Jaffe, D.; Alerhand, S.; Boye, O.; Muzafar, A.; Brossi, A. *J. Med. Chem.* **1991**, *34*, 3334.

0276-7333/92/2311-3512$03.00/0

Experimental Section

C, H, N analyses, melting point determinations, and recording of the IR and NMR spectra were performed as described elsewhere.[1] Organomercurials were prepared following previously described procedures.[2] The moieties $PhCH_2PPh_3$, $C_6H(CHO)$-6-$(OMe)_3$-2,3,4, and $C_6H(CHO)$-2-$(OMe)_3$-3,4,5 have been symbolized as Q, R, and R′, respectively.

Synthesis of $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ (1). A mixture of $Q_2[Pd_2Cl_6]$ (316 mg, 0.28 mmol) and $[HgR_2]$ (330 mg, 0.56 mmol) in acetone (15 cm^3) was stirred at room temperature for 15 h. The yellow complex **1** that precipitated was filtered, collected, and washed with acetone and diethyl ether. Yield: 354 mg, 87%. M.p.: 178 °C, dec. Λ_M (nitromethane): 117 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1670 cm^{-1}. Anal. Calcd for $C_{70}H_{66}Cl_4O_8P_2Pd_2$: C, 57.91; H, 4.58. Found: C, 57.37; H, 4.84.

Synthesis of [PdRCl(bpy)] (2). $PdCl_2$ (152 mg, 0.86 mmol) and KCl (128 mg, 1.72 mmol) were dissolved in water (15 cm^3). $[HgR_2]$ (506 mg, 0.86 mmol) and acetone (45 cm^3) were added to the aqueous solution, and the resulting mixture was stirred at room temperature for 2 h. The acetone was evaporated and further water (40 cm^3) added. In this way the mercurial [HgRCl] precipitated quantitatively and was filtered off. The resulting yellow solution was treated with 2,2′-bipyridine (134 mg, 0.86 mmol) and dichloromethane (30 cm^3). The organic layer was decanted, and the aqueous solution extracted with dichloromethane (2 × 30 cm^3). The combined extracts were dried with anhydrous $MgSO_4$ and filtered. Partial evaporation of the solution and addition of diethyl ether resulted in the precipitation of yellow **2**. Yield: 406 mg, 96%. M.p.: 177 °C dec. Λ_M (acetone): 2 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1665 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 11.11 (s, CHO, 1 H), 9.31 (br d, bpy, 1 H, J_{HH} = 5 Hz), 7.9–8.2 (m, bpy, 4 H), 7.6–7.7 (m, bpy, 2 H), 7.3 (m, bpy, +R–H, 2 H), 4.13, 4.00, and 3.90 (s, MeO, 3 H). Anal. Calcd for $C_{20}H_{19}N_2ClO_4Pd$: C, 48.70; H, 3.88; N, 5.68. Found: C, 48.80; H, 4.14; N, 5.45.

Synthesis of [PdRCl(phen)] (3). Starting from $PdCl_2$ (84 mg, 0.47 mmol), KCl (71 mg, 0.94 mmol), $[HgR_2]$ (280 mg, 0.47 mmol), and 1,10-phenanthroline (94 mg, 0.47 mmol) and workup as above gave yellow **3**. Yield: 192 mg, 79%. M.p.: 263 °C dec. Λ_M (acetone): 2 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1665. ^{1}H NMR ($CDCl_3$, δ): 11.18 (s, CHO, 1 H), 9.57 (dd, phen, 1 H, J_{HH} = 5 and 1.5 Hz), 8.57 (dd, phen, 1 H, J_{HH} = 8 and 1.5 Hz), 8.48 (dd, phen, 1 H, J_{HH} = 8 and 1.4 Hz), 7.9–8.1 (m, phen, 4 H), 7.60 (dd, phen, 1 H, J_{HH} = 5 and 6 Hz), 7.36 (s, R–H, 1 H), 4.16, 4.03, and 3.93 (s, MeO). Anal. Calcd for $C_{22}H_{19}N_2ClO_4Pd$: C, 51.09; H, 3.70; N, 5.42. Found: C, 50.77; H, 3.86; N, 5.07.

Synthesis of $[Pd_2(\eta^2\text{-}R')_2(\mu\text{-}Cl)_2]$ (4). An aqueous solution was prepared from $PdCl_2$ (86 mg, 0.49 mmol), KCl (81 mg, 1.1 mmol), and $[HgR_2]$ (290 mg, 0.49 mmol) as mentioned for complex **2** and extracted with dichloromethane (3 × 10 cm^3) after removing [HgRCl]. The combined extracts were dried over $MgSO_4$ and filtered off; the solution was evaporated and diethyl ether added giving yellow **4**. Yield: 73 mg, 44%. M.p.: 168 °C (dec. Λ_M (acetone): 1 Ω^{-1} cm^2 mol^{-1}. Molecular weight ($CHCl_3$): Calcd 674; found 668. IR: ν(CO), 1505 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 9.02 (s, CHO, 1 H), 6.41 (s, R′–H, 1 H), 4.07, 3.92, and 3.76 (s, MeO, 3 H). Anal. Calcd for $C_{40}H_{22}Cl_2O_8Pd_2$: C, 35.64; H, 3.29. Found: C, 35.03; H, 3.51.

Synthesis of [PdR′Cl(bpy)] (2′) and [PdR′Cl(phen)] (3′). Complex **4** (ca. 0.08 mmol) and stoichiometric amounts of 2,2′-bipyridine or 1,10-phenanthroline were dissolved in dichloromethane (6 cm^3) and reacted for 15 min. The solvent was evaporated and the residue recrystallized from dichloromethane/diethyl ether to give yellow **2′** or **3′**. For **2′**. Yield: 92%. M.p.: 182 °C (dec. Λ_M (nitromethane): 2 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1655 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 10.79 (s, CHO, 1 H), 9.22 (br s, bpy, 1 H), 7.9–8.2 (m, bpy, 4 H), 7.5–7.7 (m, bpy, 2 H), 7.3 (br s, bpy, 1 H), 7.14 (s, R′–H, 1 H), 3.99, 3.92, and 3.88 (s, MeO, 3 H). Anal. Calcd for $C_{20}H_{19}N_2ClO_4Pd$: C, 48.70; H, 3.88; N, 5.68. Found: C, 48.17; H, 4.11; N, 5.56. For **3′**. Yield: 84%. M.p.: 191 °C dec. Λ_M (nitromethane): 2 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1660 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 10.80 (s, CHO, 1 H), 9.48 (br d, phen, 1 H, J_{HH} = 4 Hz), 8.48 (br t, phen, 2 H, J_{HH} = 9 Hz), 7.8–7.9 (m, phen, 4 H), 7.6 (m, phen, 1 H), 7.19 (s, R–H, 1 H), 3.99, 3.91, and 3.88 (s, MeO). Anal. Calcd for $C_{22}H_{19}N_2ClO_4Pd$: C, 51.09; H, 3.70; N, 5.42. Found: C, 50.57; H, 3.87; N, 5.16.

Synthesis of $[PdR(bpy)(PPh_3)]CF_3SO_3$ (5). Complex **2** (52 mg, 0.11 mmol), PPh_3 (28 mg, 0.11 mmol), and KCF_3SO_3 (23 mg, 0.12 mmol) were reacted in acetone for 1 h. The mixture was evaporated to dryness and the residue recrystallized from dichloromethane/diethyl ether and then heated in an oven at 70 °C during 2.5 h, giving yellow **5**. Yield: 63 mg, 66%. M.p.: 143 °C. Λ_M (acetate): 117 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1670 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 10.12 (s, CHO, 1 H), 8.79 (br d, bpy, 2 H, J_{HH} = 4 Hz), 8.0–8.3 (m, bpy, 2 H), 7.3–7.7 (m, PPh_3 + bpy, 18 H), 7.04 (m, bpy, 1 H), 6.95 (s, R–H, 1 H), 3.82, 3.73, and 3.62 (s, MeO, 3 H). ^{31}P NMR ($CDCl_3$, δ): 32.2. Anal. Calcd for $C_{39}H_{34}N_2F_3O_7PPdS$: C, 53.90; H, 3.94; N, 3.22; S, 3.69. Found: C, 53.02; H, 4.17; N, 3.22; S, 3.77.

Synthesis of $[PdR'(bpy)(PPh_3)]CF_3SO_3$ (5′). This yellow compound was prepared following the procedure described for **5**, from **2′** (13 mg, 0.03 mmol), KCF_3SO_3 (6 mg, 0.03 mmol), and PPh_3 (7 mg, 0.03 mmol). The solid obtained was heated in an oven at 50 °C during 2 h. Yield: 20 mg, 85%. M.p.: 192 °C. Λ_M (acetone): 106 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1670 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 9.78 (s, CHO, 1 H), 8.65 (br d, bpy, 2 H, J_{HH} = 8 Hz), 8.15 (br t, bpy, 2 H, J_{HH} = 7 Hz), 7.0–8.0 (m, PPh_3 + bpy, 19 H), 6.90 (d, R′–H, 1 H, $^4J_{HP}$ = 3 Hz), 3.78, 3.76, and 3.67 (s, MeO, 3 H). ^{31}P NMR ($CDCl_3$, δ): 31.7. Anal. Calcd for $C_{39}H_{34}N_2F_3O_7PPdS$: C, 53.90; H, 3.94; N, 3.22; S, 3.69. Found: C, 52.85; H, 3.67; N, 3.08; S, 3.76.

Synthesis of $[PdR(bpy)(MeCN)]ClO_4$ (6). Complex **2** (82 mg, 0.17 mmol), $AgClO_4$ (34 mg, 0.17 mmol), and acetonitrile (1 cm^3) were mixed in dichloromethane (10 cm^3) and reacted for 2 h. The suspension was filtered over celite, and the resulting solution concentrated to ca. 1 cm^3; addition of diethyl ether results on the precipitation of yellow **6**. Yield: 68 mg, 67%. M.p.: 89 °C dec. Λ_M (acetone): 133 Ω^{-1} cm^2 mol^{-1}. IR: ν(CN), 2320, 2290 cm^{-1}; ν(CO), 1680 cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_3ClO_8Pd$: C, 44.17; H, 3.71; N, 7.02. Found: C, 43.51; H, 3.99; N, 6.54.

Synthesis of $[PdR(phen)(MeCN)]ClO_4$ (7). Workup as above from **3** (68 mg, 0.13 mmol) and $AgClO_4$ (27 mg, 0.13 mmol) gives yellow **7**. Yield: 68 mg, 74%. M.p.: 144 °C dec. Λ_M (acetone): 113 Ω^{-1} cm^2 mol^{-1}. IR: ν(CN), 2320, 2290 cm^{-1}; ν(CO), 1680 cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_3ClO_8Pd$: C, 46.32; H, 3.56; N, 6.75. Found: C, 46.36; H, 3.73; N, 6.61.

Synthesis of $[Pd(\eta^2\text{-}R')(bpy)]ClO_4$ (8). Complex **2′** (61 mg, 0.12 mmol) and $AgClO_4$ (26 mg, 0.12 mmol) were reacted in dichloromethane (6 cm^3)/acetonitrile (0.6 cm^3) for 2 h. The mixture was filtered off, the solution evaporated, and the residue recrystallized from dichloromethane with some drops of acetonitrile/diethyl ether to give yellow **8**. Yield: 49 mg, 73%. M.p.: 139 °C dec. Λ_M (acetone): 113 Ω^{-1} cm^2 mol^{-1}. IR: ν(CO), 1510 cm^{-1}. Anal. Calcd for $C_{20}H_{19}N_2ClO_8Pd$: C, 43.11; H, 3.43; N, 5.02. Found: C, 43.54; H, 3.77; N, 5.20.

Synthesis of $[Pd(\eta^2\text{-}R')(phen)]ClO_4$ (9). Compound **3′** (60 mg, 0.12 mmol) and $AgClO_4$ (24 mg, 0.12 mmol) were reacted in dichloromethane (10 cm^3)/acetonitrile (1 cm^3) for 2 h. The mixture was filtered off, the solution was evaporated, and the residue was stirred in acetone (see Discussion) overnight. The yellow precipitate was filtered off and dried at 70 °C for 3 h. Yield: 44 mg, 63%. M.p.: 202 °C dec. IR: ν(CO), 1505 cm^{-1}. Anal. Calcd for $C_{22}H_{19}N_2ClO_8Pd$: C, 45.56; H, 3.29; N, 4.88. Found: C, 45.30; H, 3.51; N, 4.99.

X-ray Structure Determination of Compound 2. Crystal data and numerical details of the structure are listed in Table I. A yellow needle was mounted on a glass fiber in inert oil and transferred to the cold gas stream of the diffractometer. Data were collected with monochromated Mo Kα radiation. An absorption correction was carried out (after isotropic refinement) using the program DIFABS[7] with transmission factors 0.94–1.05. Of 5201 reflections, 3492 were unique (R_{int} = 0.024) and 2417 > 4σ(F) used for all calculations (program system "Siemens SHELXTL PLUS"). The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on F. Hydrogen atoms were included using a riding

---

[6] Vicente, J.; Abad, J. A.; Stiakaki, M. A.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 137.

[7] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

Scheme I

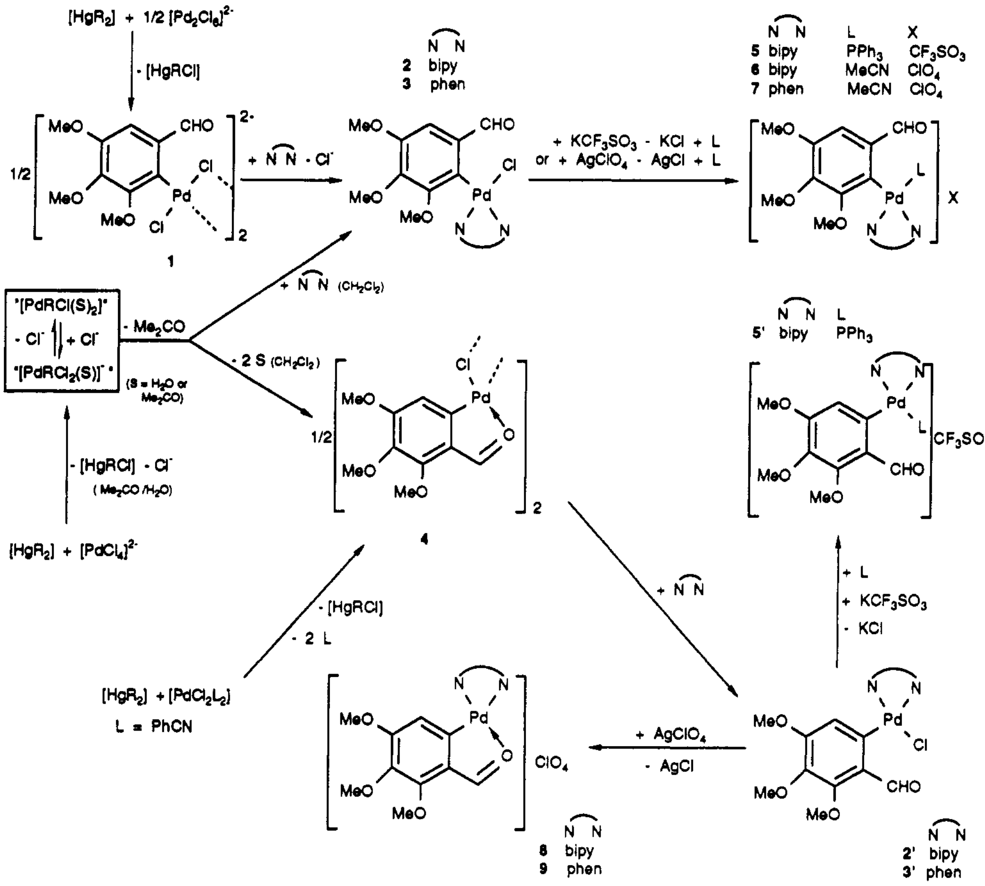


Table I. Crystal Data and Details of the Structure of Complex 2

a. Crystal Data	
formula	$C_{20}H_{19}ClN_2O_4Pd$
mw	493.2
crystal system	orthorhombic
space group	*Pbca*
Z	8
a (Å)	14.619 (4)
b (Å)	16.185 (5)
c (Å)	16.793 (5)
V (Å^3)	3973
D_x (mg·m^{-3})	1.649
F(000)	1984
μ (mm^{-1})	1.1
crystal size (mm)	0.65 × 0.15 × 0.1
b. Data Collection and Reduction	
radiatn (Å)	Mo Kα, λ = 0.71069
T (K)	178
diffractometer	Siemens R3 with LT-2 low-temp attachment
$2\theta_{max}$	50°
no. of rflns	5201
no. of unique rflns (R_{int} 0.024)	3492
no. of rflns with >4σ(*F*)	2417
c. Structure Refinement	
no. of params	262
weighting scheme	$w^{-1} = \sigma^2(F) + 0.00025F^2$
final *R*, R_w, *S*	0.030, 0.034, 1.1
max Δ/σ	0.01
max $\Delta\rho$ (e Å^{-3})	0.6

model. Final atom coordinates are given in Table II, with selected bond lengths and angles in Table III.

Results and Discussion

Synthesis and Structure of the Arylpalladium(II) Complexes. The reaction of $[HgR_2]$ (R = $C_6H(CHO)$-6,$(OMe)_3$-2,3,4 with $Q_2[Pd_2Cl_6]$ [Q = $(PhCH_2)Ph_3P$] in acetone results in the precipitation of $Q_2[Pd_2R_2Cl_2(\mu\text{-}Cl)_2]$ (1) which is easily separated from the byproduct [HgRCl] (Scheme I). 1 reacts with 2,2′-bipyridine or 1,10-

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^4) for Complex 2

	x	*y*	*z*	*U*(eq)[a]
Pd	6213.9 (2)	4755.0 (2)	3221.3 (2)	303 (1)
Cl	7515.3 (7)	4214.0 (8)	2672.8 (6)	471 (4)
N(1)	6876 (2)	5416 (2)	4135 (2)	355 (11)
N(2)	5125 (2)	5345 (2)	3723 (2)	351 (11)
C(1)	7773 (3)	5408 (3)	4301 (3)	398 (14)
C(2)	8120 (3)	5748 (3)	4995 (3)	455 (15)
C(3)	7524 (4)	6084 (3)	5533 (3)	523 (17)
C(4)	6601 (3)	6114 (3)	5360 (3)	468 (16)
C(5)	6290 (3)	5779 (3)	4643 (2)	381 (13)
C(6)	4273 (3)	5358 (3)	3440 (3)	433 (15)
C(7)	3589 (3)	5820 (3)	3781 (3)	572 (18)
C(8)	3784 (3)	6282 (3)	4438 (3)	654 (20)
C(9)	4665 (3)	6277 (3)	4748 (3)	547 (18)
C(10)	5329 (3)	5804 (3)	4381 (3)	397 (14)
C(11)	5474 (3)	4104 (3)	2448 (2)	321 (13)
C(12)	5159 (3)	3324 (3)	2640 (2)	363 (13)
C(13)	4620 (3)	2861 (3)	2123 (3)	389 (14)
C(14)	4398 (3)	3182 (3)	1368 (3)	390 (14)
C(15)	4706 (3)	3950 (3)	1158 (2)	359 (14)
C(16)	5229 (3)	4410 (3)	1692 (2)	316 (12)
C(17)	5997 (3)	2373 (3)	3432 (3)	584 (19)
C(18)	3400 (3)	2061 (3)	2624 (4)	679 (22)
C(19)	3430 (4)	3088 (4)	250 (4)	888 (27)
C(20)	5510 (3)	5250 (3)	1465 (3)	387 (13)
O(1)	5309 (2)	3009 (2)	3400 (2)	477 (11)
O(2)	4321 (2)	2080 (2)	2334 (2)	520 (11)
O(3)	3844 (2)	2693 (2)	906 (2)	509 (11)
O(4)	5303 (2)	5603 (2)	852 (2)	527 (12)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Pd–Cl	2.288 (2)	Pd–N(1)	2.107 (3)
Pd–N(2)	2.039 (3)	Pd–C(11)	1.992 (4)
C(11)–C(12)	1.382 (6)	C(11)–C(16)	1.408 (5)
C(12)–C(13)	1.392 (6)	C(12)–O(1)	1.392 (5)
C(13)–C(14)	1.408 (6)	C(13)–O(2)	1.384 (5)
C(14)–C(15)	1.369 (6)	C(14)–O(3)	1.372 (5)
C(15)–C(16)	1.394 (6)	C(16)–C(20)	1.470 (6)
C(17)–O(1)	1.440 (6)	C(18)–O(2)	1.431 (6)
C(19)–O(3)	1.410 (7)	C(20)–O(4)	1.216 (5)
Cl–Pd–N(1)	96.1 (1)	Cl–Pd–N(2)	174.3 (1)
N(1)–Pd–N(2)	79.6 (1)	Cl–Pd–C(11)	89.2 (1)
N(1)–Pd–C(11)	173.4 (1)	N(2)–Pd–C(11)	95.4 (1)
Pd–N(1)–C(1)	126.6 (3)	Pd–N(1)–C(5)	113.0 (3)
Pd–N(2)–C(10)	114.8 (3)	Pd–N(2)–C(6)	126.1 (3)
Pd–C(11)–C(12)	120.8 (3)	Pd–C(11)–C(16)	122.6 (3)
C(16)–C(20)–O(4)	125.8 (4)	C(12)–O(1)–C(17)	113.9 (3)
C(13)–O(2)–C(18)	113.9 (4)	C(14)–O(3)–C(19)	115.6 (4)

phenanthroline to give [PdRCl(bpy)] (**2**) or [PdRCl(phen)] (**3**), respectively, which are difficult to separate from the byproduct QCl; however, a better method to access these compounds free of impurities starts from $K_2[PdCl_4]$. To allow both reagents to be in solution, we reacted an aqueous solution of $K_2[PdCl_4]$ with an acetone solution of $[HgR_2]$. To our surprise, the reaction occurs without precipitation of any of the reaction products, and if acetone is removed and more water added, the byproduct [HgRCl] precipitates quantitatively leaving a yellow aqueous solution of some water-soluble arylpalladium(II) complex(es). Addition of dichloromethane solutions of 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) and extraction of the water solution with more dichloromethane allow the isolation of complexes **2** or **3**, respectively, in high yields. All of these compounds show in their IR spectra a strong band at ca. 1650 cm^{-1} assignable to ν(CO) of the formyl group. This frequency is similar to that observed in $[HgR_2]$, [HgRCl], or RH, indicating that there is no coordination of the formyl group to the metal atom.

According to these results, we assume that water-soluble species such as $[PdRCl(S)_2]$ and/or $[PdRCl_2(S)]^-$, where S = H_2O and/or Me_2CO, are present in acetone/water and in the aqueous solutions. We rule out the presence of the potassium salt of the anion of complex **1** in solution because addition of QCl does not precipitate complex **1**; all attempts to obtain complexes by concentration of these solutions failed because decomposition to palladium metal was observed during workup; moreover, for synthetic purposes they must be freshly prepared.

In an attempt to obtain palladium(II) complexes from the aqueous solutions, we extracted them with dichloromethane and obtained a complex whose elemental analyses and spectroscopic data accorded with the formulation [PdRCl] (**4**). However, the yield is always below 50%, and, from the remaining aqueous solution, complex **2** can be obtained by addition of a dichloromethane solution of 2,2′-bipyridine; the total yield based on palladium can reach 80%. Such a result may be due to a slow equilibrium between the extractable palladium(II) species (e.g. $[PdRCl(S)_2]$) and the non-extractable one (e.g. $[PdRCl_2(S)]^-$). The decomposition of the aqueous solutions prevents a better yield of **4**.

The IR spectrum of **4** shows a band attributable to ν(CO) of the formyl group at 1505 cm^{-1}; this shift to lower frequencies than those of **1**–**3** indicates the coordination of the oxygen atom of the formyl group giving rise to a cyclometalated palladium(II) complex in which tetracoordination should be completed through chloro bridging (Scheme I). The dimeric nature of complex **4** was established by a pycnometric determination in chloroform solution. However, when **4** was used as starting material for the synthesis of **2** or **3**, their isomers **2′** or **3′** were obtained instead. The primed and unprimed isomers have different spectroscopic and physical properties, which are maintained when complexes **3** and **3′** react with PPh_3 in the presence of KCF_3SO_3 to give complexes of stoichiometry $[PdR(bpy)(PPh_3)]CF_3SO_3$, **5**, and **5′**, respectively.

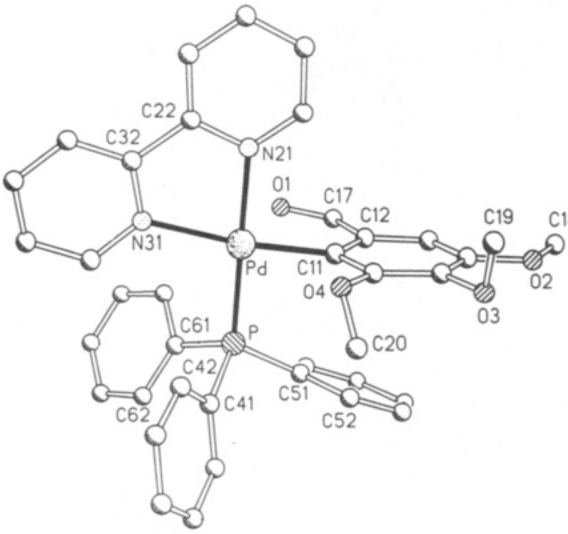


Figure 1. Crystal structure of complex **5**.

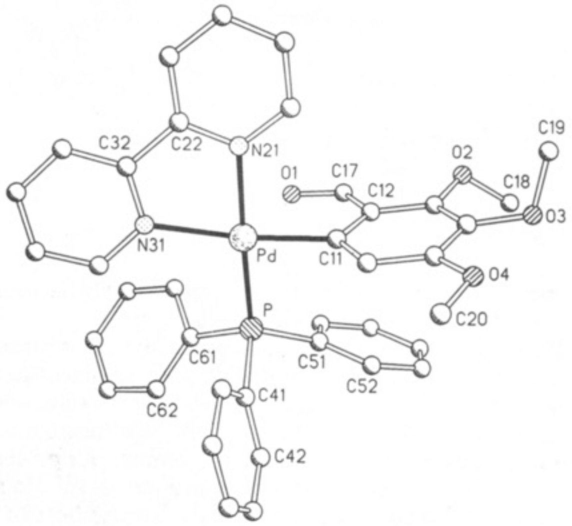


Figure 2. Crystal structure of complex **5′**.

Complex **4** can also be obtained by reacting $[HgR_2]$ with $[PdCl_2(PhCN)_2]$ (CH_2Cl_2, 0 °C, 4 h), but difficulties in the separation of the byproduct [HgRCl] (which is extracted with warm diethyl ether) lead to a maximum yield of pure **4** of approximately 50%. However, the reaction proceeds with a better yield because addition of bpy to the reaction mixture yields 67% of pure complex **2′**.

Rearrangement Processes. The isomers **5** and **5′** could be distinguished unambiguously by single crystal X-ray diffraction studies[6] (see Figures 1 and 2), revealing that complex **5** contains the original aryl ligand R, which now we have also found in the starting complex **2** (see below), whereas **5′** contains the aryl group R′ = C_6H-(CHO)-2-$(OMe)_3$-3,4,5 as the result of an unusual rearrangement of the arene substituents (see Figures 1–3). To determine at which stage of the process **4** → **2′** → **5′** the isomerization takes place, we unsuccessfully attempted to grow crystals of **4** or **2′**, but since **4** reacts with aqueous HCl to give R′H, it can be concluded that the rearrangement

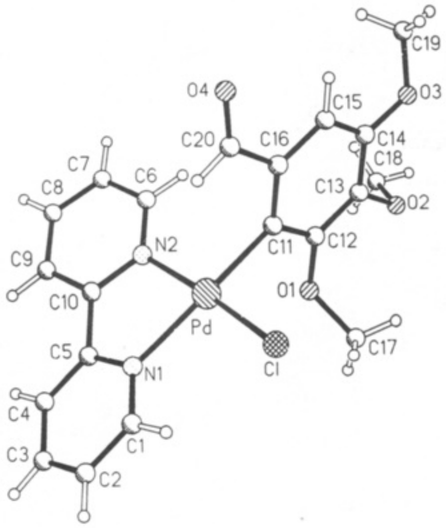
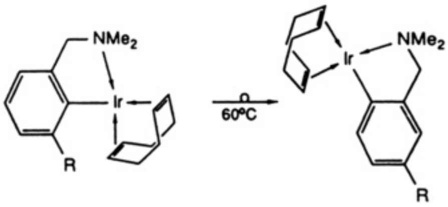


Figure 3. Crystal structure of complex 2.

Scheme II

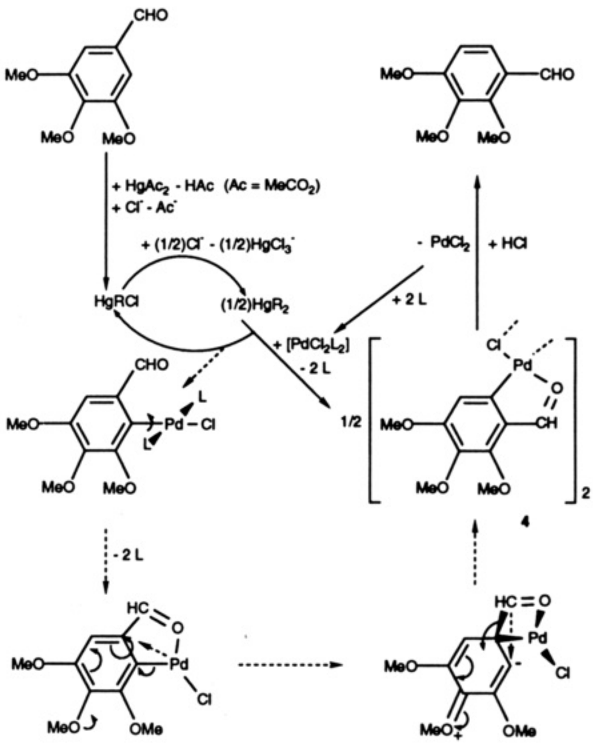


occurs on formation of **4** and, correspondingly, that complexes **2′** and **3′** also contain the R′ group.

Related rearrangements are known in arene chemistry [e.g. polyalkylbenzenes,[8] polyhalobenzenes (Jacobsen rearrangement),[9] and aromatic dicarboxylates (Henkel reaction)[10]]. However, these reactions take place at high temperatures and require catalysts, whereas our processes occur at room temperature (from the aqueous solution) or even at 0 °C from [$PdCl_2(NCPh)_2$]. To the best of our knowledge, there is only one related precedent for such metal mediated rearrangement; it has previously been reported that compounds [Ir{$C_6H_3(CH_2NMe_2)$-2-R-6}(COD)] (COD = 1,5-cyclooctadiene; R = CH_2NMe_2, Me), on heating (60 °C), rearrange to [Ir{$C_6H_3(CH_2NMe_2)$-2-R-4}(COD)]. This isomerization involves C–Ir and C–H breaking/re-forming (Scheme II). It has been shown that the driving force for this isomerization is the relief of steric crowding around the metal center.[11]

We propose that our rearrangement occurs as follows. Starting from the aqueous solution, dichloromethane probably extracts [$PdRCl(S)_2$] in which the oxygen atom of the formyl group tends to coordinate to the metal center by replacing the labile ligand S. The formation of the chelate ring coplanar with the molecular plane would force the observed rearrangement in order to avoid the repulsion between the 2-MeO group and the ligand trans to the coordinated oxygen atom, whereas the R group in all complexes where the ligands in cis position are not so labile (e.g. **1**–**3**) can easily be accommodated perpendicular to the molecular plane. We assume that a three-coordinate intermediate [PdRCl] could be formed as postulated in the case of the iridium-mediated isomerization (Scheme III). If S = H_2O, this process should be favored due to the low solubility of water in dichloromethane, while in aqueous solutions the isomerization is not observed because chelation from [$PdRCl(S)_2$]$_{(H_2O)}$ is disfavored. If bpy or phen are present in the dichloromethane used to extract the aqueous solution, complexes **2** or **3** are formed instead of **2′** or **3′** because their formation is faster than the rearrangement process. In addition, the yields are higher than that of **4** because the ligands react with [$PdRCl(S)_2$]$_{(Cl_2CH_2)}$ and with all the arylpalladium(II) species present in aqueous solution, giving **2** or **3** which are extracted with dichloromethane. Starting from [$PdCl_2(NCPh)_2$], it is reasonable to assume that the R group of the product of the transmetalation reaction, [$Pd(R)Cl(NCPh)_2$], also tends to rearrange by replacing the labile PhCN ligand.

Scheme III. Proposed Pathway (- -) for the Rearrangement Process (—)



In these rearrangement processes, electronic effects should not be neglected: in the isomerized aryl group, the methoxy groups release more electron density to the formyl group favoring its coordination to the palladium atom.

Two noteworthy features of our rearrangement reactions are, firstly, the substituent migrations under very mild conditions and, secondly, with respect to the iridium-mediated isomerizations,[11] the involvement of C–C bond activation. At the moment, we cannot propose any mechanism for this reaction, since the non-isomerized intermediates have not been detected. However, we believe that, as has been shown for the iridium reaction, our rearrangement is *intramolecular* and that, in addition to steric effects, the methoxy groups, in particular the para substituent, play some electronic role. Scheme III summarizes the complete series of reactions for the isomerization of $HC(O)C_6H_2(OMe)_3$-3,4,5 to $HC(O)C_6H_2(OMe)_3$-2,3,4 and attempts to give a possible pathway for the rearrangement process.

Additional evidence for the severe steric hindrance that the 2-methoxy substituent exerts in the R group is shown

---

[8] Baddeley, G.; Holt, G.; Voss, D. *J. Chem. Soc.* **1952**, 100. McCaulay, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1952**, *74*, 6246. Brown, H. C.; Jungk, H. *J. Am. Chem. Soc.* **1955**, *77*, 5579.

[9] Smith, L. I. *Organic Reactions*; Adams, R., Bachman, W. E., Fieser, L. F., Johnson, R. J., Snyder, H. R., Eds.; Wiley: New York, 1942; Vol. 1, Chapter 12.

[10] Raecke, B. *Angew. Chem.* **1958**, *70*, 1.

[11] Van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Nordemann, R. A.; Spek, A. L. *Organometallics* **1988**, *7*, 1549.

Organometallics 1992, *11*, 3517-3525

by the different behavior of complexes 2 and 3 with respect to their isomers 2′ and 3′ when they react with $AgClO_4$ in the presence of acetonitrile. The former give $[PdR(bpy)(MeCN)]ClO_4$ (6) and $[PdR(phen)(MeCN)]ClO_4$ (7), respectively, while the latter gives the cyclometalated $[Pd(\eta^2\text{-}R')(bpy)]ClO_4$ (8) [ν(CO), 1510 cm^{-1}] and $[Pd(\eta^2\text{-}R')(phen)]ClO_4$ (9) [ν(CO), 1505 cm^{-1}], respectively, although, in the last case, a mixture of 9 and some species containing MeCN (by IR), presumably $[PdR'(phen)(MeCN)]ClO_4$, was initially obtained; however, stirring this mixture in acetone removes MeCN, yielding pure 9. The low solubilities of 6–9, as well as 1, have prevented measurements of their NMR spectra.

Crystal Structure of Complex 2. Figure 3 shows the expected tetracoordination of the metal center. The geometry at Pd is not exactly planar, because the atom N(2) lies 0.22 Å out of the plane of Pd, C(11), Cl, and N(1). The dihedral angle between the rings of the bpy ligand is 12°. Its bite angle is 79.6°. The Pd–N bond distances (Table III) show a clear difference in the trans influences of the aryl [Pd–N(1), 2.107 (3) Å] and chloro ligands [Pd–N(2), 2.039 (3) Å]; both are significantly shorter than those found[6] in the cationic complexes 5 and 5′ [2.143 (4), 2.137 (3) Å and 2.099 (4), 2.114 (3) Å, respectively] which can be explained as a consequence of greater Pd to N π-back-bonding in neutral complex 2 than in cationic 5 and 5′. This difference is probably also responsible for the different orientation of the formyl group with respect to the palladium atom; in 5 and 5′ the formyl oxygen makes a short contact to Pd (2.921 (5) and 2.926 (3) Å, respectively) whereas in 2 the hydrogen atom is involved (Pd⋯H, 2.70 Å). All these formally nonbonded distances are appreciably longer than expected values for covalent bonds (Pd–O, 2.2 Å; Pd–H, 1.6 Å).[12] The Pd–C bond distance (1.992 (4) Å) is similar to those in 5 (2.010 (5) Å) and 5′ (1.986 (3) Å).

Acknowledgment. We thank the Fonds der Chemischen Industrie and Dirección General de Investigación Científica y Técnica (Grant PB89-0430) for financial support.

Supplementary Material Available: Complete listings of bond lengths and angles, anisotropic displacement parameters, and H atom coordinates (4 pages). Ordering information is given on any current masthead page.

OM9202128

---

[12] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(Aryne)metallocene- and (Alkyne)metallocene-Derived Dimetallic Zirconium/Aluminum Complexes Containing Planar-Tetracoordinate Carbon

Gerhard Erker* and Markus Albrecht

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-4400 Münster, Germany

Carl Krüger, Stefan Werner, Paul Binger, and Franz Langhauser

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a. d. Ruhr, Germany

Received April 21, 1992

Compounds X-$[M^2]$ of Lewis acidic main group metals can be added to very reactive alkyne–transition metal complexes $(\eta^2\text{-}RC{\equiv}CR)[M^1]$ to form dimetallabicyclic organometallic compounds $[M^1](\mu\text{-}\eta^1{:}\eta^2\text{-}RCCR)(\mu\text{-}X)[M^2]$ containing a planar-tetracoordinate carbon atom, which is stabilized by the combined σ-donor/π-acceptor properties of the specific metal/ligand combination. This general synthetic scheme has been used to prepare such planar-tetracoordinate carbon complexes by reacting e.g. $(\eta^2\text{-aryne})(PMe_3)ZrCp_2$ (12) with 2 molar equiv of diisobutylaluminum hydride. Initial $Me_3P{\cdot}HAl(iBu)_2$ adduct formation generates the reactive $(\eta^2\text{-aryne})ZrCp_2$ intermediate, which is then trapped by additional hydridoaluminum reagent to yield the thermodynamically stable complex $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}H)Al(iBu)_2$ (14a). Complex 14a crystallizes in space group $P2_1/n$ with cell parameters a = 16.749 (3) Å, b = 13.833 (1) Å, c = 20.178 (2) Å, β = 90.74 (1)°, R = 0.088, and R_w = 0.093. It contains a planar-tetracoordinate carbon center [C(2)] at the bridgehead position of the dimetallabicyclic framework which is bonded to two carbon atoms [d(C(2)–C(1)) = 1.37 (2) Å, d(C(2)–C(3)) = 1.41 (1) Å], the zirconium [d(C(2)–Zr) = 2.430 (8) Å], and the aluminum atom [d(C(2)–Al) = 2.09 (1) Å, all values averaged over the two independent molecules; the sum of bonding angles around C(2) is 360°]. The reaction between 12 and trimethylaluminum gave the analogously structured $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_3)AlMe_2$ complex 14b; treatment of 12 with triethylaluminum furnished $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_2CH_3)AlEt_2$ (14c). Complex 14b was characterized by X-ray diffraction (space group $P2_1/n$, a = 9.151 (1) Å, b = 14.022 (1) Å, c = 14.415 (1) Å, β = 104.56 (1)°, R = 0.042, R_w = 0.057). Again, carbon atom C(2) is planar-tetracoordinate [d(C(2)–C(1)) = 1.383 (4), d(C(2)–C(3)) = 1.423 (5), d(C(2)–Zr) = 2.481 (3), d(C(2)–Al) = 2.082 (3) Å; the sum of bonding angles at C(2) is 360°]. The general synthetic scheme for the preparation of dimetallabicyclic "anti-van't Hoff/LeBel compounds" can also be applied to reaction sequences starting from stable $(\eta^2\text{-alkyne})$metallocene complexes. Thus, the reaction of $(\eta^2\text{-cyclohexyne})(PMe_3)ZrCp_2$ (11a) or $(\eta^2\text{-diphenylacetylene})(PMe_3)ZrCp_2$ (11b) with excess trimethylaluminum gave the respective $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}RCCR)(\mu\text{-}CH_3)AlMe_2$ products (7d,e). The reaction between the (tolane)metallocene complex 11b with a mixture of 9-BBN and triethylboron produced $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}PhCCPh)(\mu\text{-}H)BEt_2$ (15) in low yield.

Since 1874, when van't Hoff's and LeBel's pioneering and imaginative thoughts and conclusions were independently published, it is well-known that tetracoordinate carbon in organic compounds favors a tetrahedral coor-

0276-7333/92/2311-3517$03.00/0