

Supporting information (I)

Diverse Pathways on the Reaction of Fischer Carbenes and Palladium

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Experimental Section

General procedure. ^1H NMR and ^{13}C NMR spectra were recorded at 22 °C on Bruker Avance 500 (500.1 and 125.7 MHz), 300 (300.1 and 75.4 MHz) or Bruker 200-AC (200.1 and 50 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^1H , 0.0 ppm) and CDCl_3 (^{13}C , 77.0 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer. DMF and CH_3CN were distilled from calcium hydride and THF from sodium-benzophenone. Flame-dried glassware and standard Schlenk techniques were used for moisture sensitive reactions. Merck silica-gel (230-400 Mesh) or fluorisil was used as the stationary phase for purification of crude reaction mixtures by flash column chromatography. Identification of products was made by TLC (kiesegel 60F-254). UV light ($\lambda = 254\text{ nm}$) and 5% phosphomolybdic acid solution in 95% EtOH were used to develop the plates.

All commercially available compounds were used without further purification. Carbene complex pentacarbonyl[1-ethoxy-3-phenyl-2-propinyliden]chromium(0) **6**, was prepared according to literature methods.¹

Synthesis of carbene complex 5a. A solution of 210 mg (2.25 mmol) of aniline and 790 mg (2.25 mmol) of carbene complex **6** in THF was stirred for 12 h at room temperature to yield 998 mg (100 %) of complex **5a** as an orange-red solid. ^1H NMR (CDCl_3 , 300 MHz): $\delta = 1.68$ (t, $J = 7.0\text{ Hz}$, 3H), 4.99 (q, $J = 7.0\text{ Hz}$, 2H), 6.63 (s, 1H), 6.69 (d, $J = 7.8\text{ Hz}$, 2H), 7.04-7.41 (m, 8H), 10.47 (bs, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 15.8, 74.4, 122.1, 122.8, 125.3, 128.7, 129.0, 129.1, 130.3, 134.8, 138.3, 147.0, 218.2, 224.0, 301.9$. IR (KBr): $\nu = 3423, 2047, 1964, 1902, 1554\text{ cm}^{-1}$; $\text{C}_{22}\text{H}_{17}\text{CrNO}_6$: calcd C, 59.60; H, 3.86; Cr, 11.73; N, 3.16; found C, 59.56; H, 3.90.

Synthesis of carbene complex 5b. A solution of 313 mg (1.43 mmol) of *o*-iodoaniline and 500 mg (1.43 mmol) of carbene complex **6** in THF was stirred for 36 h at room temperature to yield 800 mg (98 %) of complex **5b** as an orange-red solid. ¹H NMR (CDCl₃, 300 MHz): δ = 1.76 (t, *J* = 7.0 Hz, 3H), 5.10 (q, *J* = 7.0 Hz, 2H), 6.46 (d, *J* = 6.0 Hz, 1H), 6.75 (m, 2H), 6.95 (m, 1H), 7.27-7.38 (m, 5H), 7.83 (d, *J* = 6.0 Hz, 1H), 10.01 (bs, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ = 16.3, 75.5, 93.1, 123.0, 126.0, 126.8, 128.5, 128.7, 129.0, 130.3, 134.9, 139.3, 140.6, 145.3, 218.0, 224.1, 306.1. IR (CCl₄): ν 3463, 2050, 1969, 1924, 1899, 1569, 1541 cm⁻¹; C₂₂H₁₆CrINO₆: calcd C, 46.42; H, 2.83; Cr, 9.13; I, 22.29; N, 2.46; found C, 46.30; H, 2.86.

Stoichiometric reactions of enamine carbene complexes with palladium catalysts.

General method. A solution of the corresponding carbene complex and the palladium catalysts in a 1:0.6 ratio respectively were dissolved in MeCN together with K₂CO₃ in excess at room temperature. The mixture was stirred under argon atmosphere as indicated for each case at room temperature. Then, the solvent was eliminated in vacuo and the residue obtained disaggregated in AcOEt and filtered over a short pad of celita. For reactions with DMF as solvent, water was added to the reaction mixture and was extracted with AcOEt. The organic layers were washed with brine and dried over magnesium sulphate. The solvent was removed in vacuo. Further purification by flash column chromatography allowed the isolation of pure compounds.

Stoichiometric reactions of complex 5a.

a) PdCl₂(MeCN)₂/K₂CO₃ in MeCN. Following the general method, from a solution of 25 mg (0.06 mmol) of carbene complex **5a**, 88 mg (0.03 mmol) of PdCl₂(MeCN)₂, and 39 mg (0.28 mmol) of K₂CO₃ in 1 mL of MeCN, after 2 h were obtained 17 mg (93 %) of **7a**. ¹H NMR (CDCl₃, 200 MHz): δ = 1.50 (t, *J* = 7.1 Hz, 6H), 4.05 (q, *J* = 7.1 Hz,

4H), 5.45 (s, 2H), 6.31-6.36 (m, 4H), 6.53-6.57 (m, 6H), 6.92-6.95 (m, 4H), 7.05-7.09 (m, 6H); ^{13}C NMR (CDCl_3 , 50 MHz): δ = 14.6, 65.1, 109.7, 123.2, 124.3, 127.4, 127.7, 127.9, 128.0, 137.3, 148.1, 182.1, 208.5; IR (KBr): ν = 3028, 1479, 1454, 1437, 1198 cm^{-1} . HRMS (FAB): calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_2\text{O}_2$ ^{104}Pd 605.1582; found: 605.1566.

b) $\text{Pd}(\text{OAc})_2/\text{K}_2\text{CO}_3$ in MeCN. Following the general method, from a solution of 25 mg (0.06 mmol) of carbene complex **5a**, 8 mg (0.034 mmol) of $\text{Pd}(\text{OAc})_2$, and 39 mg (0.28 mmol) of K_2CO_3 in 1 mL of MeCN, after 4.5 hours were obtained 5 mg (27%) of palladium carbene complex **7a**, 2.1 mg (16%) of aldehyde **9a** and 2 mg (12%) of the ester **8a**. The same reaction using 62 mg (0.11 mmol) of KOH, instead of K_2CO_3 , gives 3 mg (19%) of palladium carbene complex **7a**, 13 mg (55%) of aldehyde **9a** and 2.3 mg (14%) of ester **8a**. **Aldehyde 9a:** ^1H NMR (CDCl_3 , 200 MHz): δ = 5.38 (d, J = 2.5 Hz, 1H), 6.75 (m, 1H), 6.79 (m, 1H), 7.01-7.05 (m, 2H), 7.13-7.17 (m, 2H), 7.31-7.39 (m, 4H), 9.31 (d, J = 2.5 Hz, 1H), 12.34 (bs, 1H); ^{13}C NMR (CDCl_3 , 50 MHz): δ = 100.7, 123.3, 124.5, 128.3, 128.5, 128.7, 129.8, 134.6, 139.0, 161.0, 188.0; IR (CHCl_3): ν = 3018, 1599, 1568, 1215 cm^{-1} ; **Ester 8a:** ^1H NMR (CDCl_3 , 300 MHz): δ = 1.33 (t, J = 7.1 Hz, 3H), 4.22 (q, J = 7.1 Hz, 2H), 5.00 (s, 1H), 6.66-6.69 (m, 2H), 6.89-6.94 (m, 1H), 7.06-7.11 (m, 2H), 7.28-7.35 (m, 5H), 10.30 (bs, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ = 14.0, 59.3, 91.2, 122.2, 122.9, 128.2, 128.4, 128.6, 129.4, 136.0, 140.4, 159.1, 170.1; IR(CHCl_3): ν = 3018, 1288, 1215, 1180 cm^{-1} .

c) $\text{Pd}(\text{OAc})_2/\text{K}_2\text{CO}_3$ in DMF. Following the general method, from a solution of 25 mg (0.06 mmol) of carbene complex **5a**, 8 mg (0.034 mmol) of $\text{Pd}(\text{OAc})_2$, and 39 mg (0.28 mmol) of K_2CO_3 in 1 mL of DMF, after 6 hours the aldehyde **9a** was observed as the main product in the reaction mixture..

d) PdCl₂/K₂CO₃ in MeCN. Following the general method, from a solution of 25 mg (0.06 mmol) of carbene complex **5a**, 6 mg (0.03 mmol) of PdCl₂, and 39 mg (0.28 mmol) of K₂CO₃ in 1 mL of MeCN, after 1h and 35 minutes were isolated 7 mg (38%) of palladium carbene complex **7a**.

e) Pd(PPh₃)₄/K₂CO₃ in MeCN. Following the general method, from a solution of 25 mg (0.06 mmol) of carbene complex **5a**, 39 mg (0.03 mmol) of Pd(PPh₃)₄, and 39 mg (0.28 mmol) of K₂CO₃ in 1 mL of MeCN after 3 hours were obtained 5 mg (27%) of palladium carbene complex **7a**, 3 mg (22%) of aldehyde **9a** and 5 mg (31%) of ester **8a**.

Stoichiometric reactions of complex 5b.

a) PdCl₂(MeCN)₂/K₂CO₃ in MeCN. Following the general method, from a solution of 25 mg (0.044 mmol) of **5b**, 7 mg (0.03 mmol) of PdCl₂(MeCN)₂ and 30 mg (0.22 mmol) of K₂CO₃ in 1 mL of MeCN, after 90 minutes were obtained 17 mg (90%) of pure **7b**. Further crystallization in a mixture of CH₂Cl₂/pentane gave **7b** as yellow crystals. ¹H NMR (CDCl₃, 500 MHz): δ = 1.52 (t, *J* = 7 Hz, 6H), 4.09 (q, *J* = 7 Hz, 4H), 5.50 (s, 2H), 6.21-6.27 (m, 2H), 6.52-6.63 (m, 4H), 6.93-7.00 (m, 6H), 7.05-7.28 (m, 6H); ¹³C NMR (CDCl₃, 125 MHz): δ = 14.6, 65.3, 98.7, 109.4, 125.0, 126.3, 127.1, 127.4, 127.5, 128.1, 137.1, 137.5, 148.2, 181.6, 210.0; IR (CHCl₃): ν = 3018, 2927, 2854, 1479, 1452, 1437, 1215, 1197 cm⁻¹. HRMS (FAB): calcd. for C₃₄H₃₁I₂N₂O₂¹⁰⁴Pd 856.9523; found: 856.9515.

b) Pd(PPh₃)₄/K₂CO₃ in DMF. Following the general method from a solution of 50 mg (0.09 mmol) of carbene complex **5b**, 61 mg (0.05 mmol) of Pd(PPh₃)₄, and 61 mg (0.44 mmol) of K₂CO₃ in 2 mL of DMF after 26 hours and were obtained 7 mg (20 %) of ester **8b** and 10 mg (42%) of the indole **11**. **Ester 8b:** ¹H NMR (CDCl₃, 300MHz): δ = 1.34 (t, *J* = 7.1 Hz, 3H), 4.26 (c, *J* = 7.1 Hz, 2H), 5.14 (s, 1H), 6.33-6.36 (m, 1H), 6.61-6.67 (m, 1H), 6.87-6.92 (m, 1H), 7.25-7.36 (m, 5H), 7.78-7.81 (m, 1H), 10.13 (bs, 1H);

^{13}C NMR (CDCl_3 , 50 MHz): δ = 14.5, 59.5, 93.0, 93.1, 124.2, 124.6, 128.0, 128.1, 128.5, 129.5, 135.7, 139.1, 142.0, 158.1, 169.7; IR (CHCl_3): ν = 3018, 1612, 1599, 1288, 1215, 1177, 752 cm^{-1} ; $\text{C}_{17}\text{H}_{16}\text{NO}_2$: calcd C, 50.41; H, 4.23; N, 3.67; found C, 50.45; H, 4.21. **Indole 11**:³ ^1H NMR (CDCl_3 , 300 MHz): δ = 1.31 (t, J = 7.0 Hz, 3H), 4.33 (q, J = 7.0 Hz, 2H), 7.27-7.47 (m, 6H), 7.66-7.70 (m, 2H), 8.23-8.25 (m, 1H), 8.50 (bs, 1H); ^{13}C NMR (CDCl_3 , 75 MHz): δ = 14.3, 59.7, 104.8, 111.0, 122.1, 122.2, 123.2, 127.6, 128.1, 129.2, 129.6, 132.0, 135.1, 144.4, 165.3; IR (CCl_4): ν = 3271, 1670, 1429, 1489, 1126, 1049 cm^{-1} ; MS-EI m/z (%): 265 (75), 220 (100), 221 (19), 193 (40), 165 (29).

c) $\text{Pd}(\text{PPh}_3)_4$ in DMF. Following the general method, from a solution of 50 mg (0.09 mmol) of carbene complex **5b** and 61 mg (0.05 mmol) of $\text{Pd}(\text{PPh}_3)_4$ in 2 mL of DMF after 20 hours and were obtained 2 mg (6 %) of ester **8b**, 11 mg (48%) of the indole **11**, and 9 mg (40%) of quinoline **10**. **Quinoline 10**:⁴ ^1H NMR (CDCl_3 , 200 MHz): δ = 1.55 (t, J = 7.0 Hz, 3H), 4.30 (q, J = 7.0 Hz, 2H), 7.09 (s, 1H), 7.39-7.69 (m, 5H), 8.01-8.19 (m, 4H). ^{13}C NMR (CDCl_3 , 50 MHz): δ = 14.6, 64.1, 98.6, 120.5, 121.7, 125.3, 127.6, 128.7, 129.1, 129.2, 130.0, 140.4, 149.2, 158.8, 162.2; IR (CHCl_3): ν = 1652, 1593, 1558, 1506, 1215 cm^{-1} ; ESI-MS: $[\text{C}_{17}\text{H}_{15}\text{NO} + \text{H}^+]$ 250; MS-EI m/z (%): 249 (100), 234 (33), 221 (72), 220 (66), 193 (36), 165 (28). $\text{C}_{17}\text{H}_{15}\text{NO}$: calcd C, 81.90; H, 6.06; N, 5.62; found C, 82.12; H, 6.27.

c) $\text{Pd}(\text{PPh}_3)_4/\text{K}_2\text{CO}_3$ in MeCN. Following the general method, from a solution of 50 mg (0.09 mmol) of carbene complex **5b**, 61 mg (0.05 mmol) of $\text{Pd}(\text{PPh}_3)_4$, and 61 mg (0.44 mmol) of K_2CO_3 in 2 mL of MeCN, after 24 hours and were obtained 14 mg (40 %) of ester **8b** and 8 mg (33%) of the indole **11**.

Catalytic Reactions of enamine carbene complex 5b with palladium catalysts. A solution of the carbene complex **5b** and the palladium catalysts in a 1:0.3 or 1:0.1 ratio

respectively were dissolved in MeCN or DMF together with K_2CO_3 in excess at room temperature. The mixture was stirred under argon atmosphere as specified for each case at room temperature. Then, for reactions carried out in MeCN, the solvent was eliminated in vacuo and the residue obtained disaggregated in AcOEt and filtered over a short pad of celite. For reactions in DMF, water was added to the reaction mixture that was further extracted with AcOEt. The organic layers were washed with brine and dried over magnesium sulphate and the solvent removed in vacuo. Further purification by flash column chromatography allowed getting pure compounds.

a) 10% of $Pd(OAc)_2/K_2CO_3$ in MeCN. Following the general method from a solution of 250 mg (0.44 mmol) of carbene complex **5b**, 10 mg (0.044 mmol) of $Pd(OAc)_2$, and 303 mg (2.2 mmol) of K_2CO_3 in 10 mL of MeCN after 7 days were obtained 16 mg (8%) of palladium carbene complex **7b**, 21 mg (27%) of aldehyde **9b** and 33mg (38%) of ester **8b**. **Aldehyde 9b:** 1H NMR ($CDCl_3$, 200MHz): δ = 5.46 (d, J = 2.3 Hz, 1H), 6.47 (m, 1H), 6.72 (m, 1H), 6.94 (m, 1H), 7.25-7.41 (m, 5H), 7.83 (m, 1H), 9.39 (d, J = 2.3 Hz, 1H), 12.07 (bs, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 94.2, 101.5, 126.2, 126.3, 128.2, 128.3, 128.5, 130.0, 134.5, 139.3, 141.3, 160.5, 188.6; IR (KBr): ν = 2816, 2741, 1618, 1605, 1585, 1560, 1500 cm^{-1} ; $C_{15}H_{12}INO$: calcd C, 51.60; H, 3.46; N, 4.01; found C, 51.88; H, 3.37.

b) 30% of $Pd(OAc)_2/K_2CO_3$ in MeCN. Following the general method, from a solution of 250 mg (0.44 mmol) of carbene complex **5b**, 30 mg (0.044 mmol) of $Pd(OAc)_2$, and 304 mg (2.2 mmol) of K_2CO_3 in 10 mL of MeCN, after 12 h were obtained 40 mg (21%) of palladium carbene complex **7b** and 21 mg (14%) of aldehyde **9b**.

c) 30% of $Pd(OAc)_2/K_2CO_3$ in DMF. Following the general method, a solution of 250 mg (0.44 mmol) of carbene complex **5b**, 30 mg (0.044 mmol) of $Pd(OAc)_2$ and 304 mg (2.2 mmol) of K_2CO_3 in 10 mL of DMF was stirred for 12 h. After extraction and

solvent elimination, the residue obtained was dissolved in 50 mL of (1:1) hexane:AcOEt and exposed to sunlight for 8 h and then, filtered over a short pad of celite. The products obtained were separated by flash column chromatography on silica gel to give 54 mg (49 %) of quinoline **10** and 44 mg (38%) of indole **11**.

Reaction of Palladium Carbene Complex 7b in THF. A solution of 29 mg (0.03 mmol) of palladium carbene complex **7b** in 2 mL of THF was heated in a bath at 30°C, 40°C and 50°C. In all cases, after 2 days complex **7b** was recovered unaltered.

Reaction of Palladium Carbene Complex 7b with UV/visible light/air. A solution of 50 mg (0.06 mmol) of palladium carbene complex **7b** in a mixture of 25 mL of hexane and 25 mL of AcOEt was exposed to sunlight for 8 hours. Complex **7b** was recovered unaltered. Then the same solution was irradiated through Pyrex with a 400 W medium-pressure mercury lamp for 5 days. Again complex **7b** was recovered unaltered.

Reaction of Palladium Carbene Complex 7b with CAN. To a solution of 50 mg (0.06 mmol) of palladium carbene complex **7b** in 3.5 mL of MeCN at –20°C were added slowly a solution of 102 mg (0.18 mmol) of CAN in 1.4 mL. The temperature was up to –5°C for 30 minutes and 5 mL of water were added. The solution was stirred at room temperature for 10 minutes. The reaction mixture was extracted with AcOEt and the organic layers were washed with water, dried over magnesium sulphate and the solvent removed in vacuo to yield a complex mixture of unidentified products.

Reaction of Palladium Carbene Complex 7b with iodine. To a solution of 13 mg (0.015 mmol) of palladium carbene complex **7b** in 8.5 mL of MeCN were added 4 mg (0.015 mmol) of iodine. The solution was stirred at room temperature for 5 minutes. After removing the solvent in vacuo a complex mixture of unidentified products was obtained.

Reaction of Palladium Carbene Complex 7b with Et₃N. To a solution of 20 mg (0.023 mmol) of palladium carbene complex **7b** in 4 mL of DMF were added 0.1 mL (0.093 mmol) of Et₃N. The solution was stirred at room temperature for 25 hours. Then 0.1 mL of Et₃N were added again. After 2 days, complex **7b** was recovered unaltered.

Reaction of Palladium Carbene Complex 7b with PMe₃. To a solution of 5.4 mg (0.006 mmol) of palladium carbene complex **7b** in 1 mL of CH₂Cl₂ was added a drop of PMe₃. The solution was stirred at room temperature for 2 days. Complex **7b** was recovered.

Reaction of Palladium Carbene Complex 7a with H₂SO₄ (10%). Over a solution of 134 mg (0.22 mmol) of palladium carbene complex **7a** in 38 mL of THF was added 1 mL H₂SO₄ (10%). After 5 minutes water was added to the reaction mixture that was further extracted with CH₂Cl₂. The organic layers were washed with NaHCO₃, water, and dried over magnesium sulphate. Then, the solvent removed in vacuo and the products obtained were separated by flash column chromatography on silica gel to give 6 mg (28 %) of benzoyl ethyl acetate. ¹H NMR (CDCl₃, 200 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3H), 4.00 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 7.45-7.98 (m, 5H); ¹³C NMR (CDCl₃, 50 MHz): δ = 14.1, 46.0, 61.4, 126.1, 128.5, 128.8, 133.7, 167.5, 192.5; IR (CH₂Cl₂): ν = 2981, 1737, 1688 cm⁻¹.

X-Ray Crystal Analysis Structure of complex 7b. Crystal data: $C_{34}H_{30}I_2N_2O_2Pd$, molecular mass = 858.80, monoclinic, $P2(1)/c$, $a = 16.8655(9)\text{\AA}$, $b = 12.4380(6)\text{\AA}$, $c = 16.0200(8)\text{\AA}$, $\beta = 94.150(1)^\circ$, $V = 3351.8(3)\text{\AA}^3$, $Z = 4$, $D_c = 1.702\text{ Mg/m}^3$, $F(000) = 1664$, $\mu = 2.427\text{ mm}^{-1}$. Data collection: SMART CCD-BRUKER diffractometer, with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) operating at 50kV and 25mA. The intensity data were collected over an hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 20s covered 0.3 in ω . Reflection range for the data collection were $1.21^\circ < \theta < 28.95^\circ$. A 8322 independent reflections were measured and 4301 were considered observed [$I > 2\sigma(I)$ criterium]. Structure solution and refinement: The structure was solved by direct methods. The refinement was done by full matrix least-squares procedures on F^2 (SHELXTL version 5.1).⁵ The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated position and refined riding on the respective carbon bonded atoms. Final $R(R_w)$ value was 3.80(9.54).

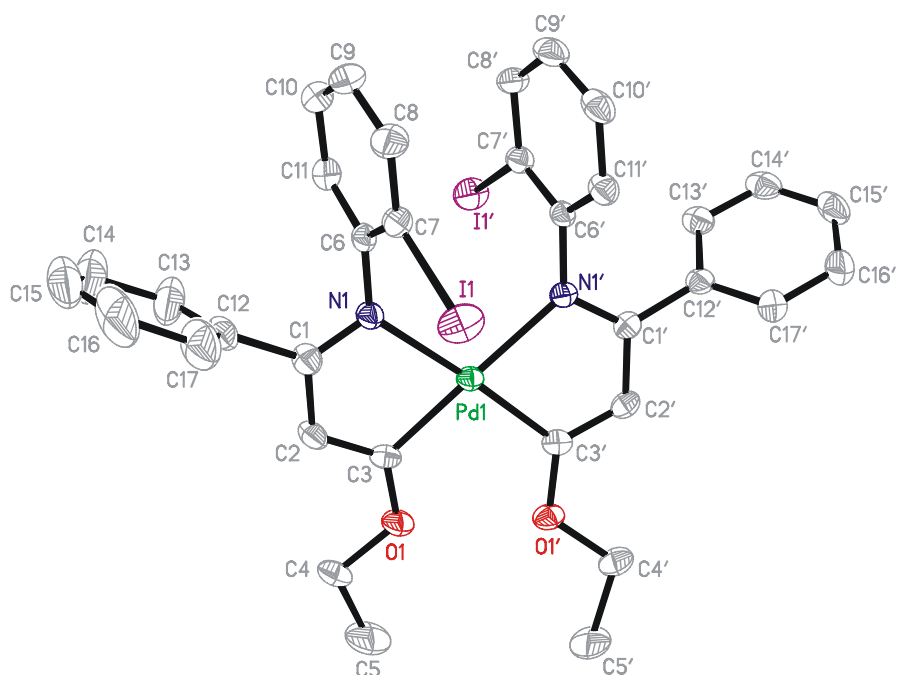


Figure 1. ORTEP drawing of *bis*-palladacarbene **7b**. The geometry around the Pd1 is almost square planar. Selected bond lengths [\AA] and angles [deg]: Pd1-N1 2.164(4), Pd1-N1' 2.145(4), Pd1-C3 1.994(4), Pd1-C3' 1.984(4), C3-O1 1.339(5), O1-C4 1.444(5), C3'-O1' 1.334(5), O1'-C4' 1.452(5), N1-Pd1-C3 79.2(2), C3-Pd1-C3' 98.3(2), C3'-Pd1-N1' 79.1(2) and N1'-Pd1-N1 103.8(1).

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