Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 576–578

Synthesis, structure and catalytic properties of Pd^{II}-based bimetallic complexes with ferrocenecarboxylic acid

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Syntheses of complexes **1** *and* **2**. Complexes $[Pd(lut)_2(OAc)_2]$ were prepared as reported in Ref. 14 of the main text. To a solution of $[Pd_3(OAc)_6]$ (0.9 mmol, 0.19 g) in benzene (25 ml) was added the corresponding 2,6- or 3,4-lutidine (1.8 mmol, 0.2 ml). The solution was left for crystallization under slow evaporation, while the colour of the solution changed to light yellow. Crystals suitable for XRD were formed after several days. The precipitated $[Pd(lut)_2(OAc)_2]$ was dried *in vacuo*.

Complex $[Pd(2,6\text{-lut})_2(FcCOO)_2]$ **3**. To a solution of $[Pd(2,6\text{-lut})_2(OAc)_2]$ (0.1 mmol, 43.8 mg) in CH_2Cl_2 (7 ml) and MeOH (3 ml) was added a solution of FcCOOH (0.2 mmol, 46 mg) in CH_2Cl_2 (27 ml). The solution was dried under reduced pressure, and green-brown solid was collected.
Complex $[Pd(3,4\text{-lut})_2(FcCOO)_2]$ **4**. To a solution of $[Pd(3,4\text{-lut})_2(OAc)_2]$ (0.1 mmol, 43.8 mg) in CH_2Cl_2 (7 ml) was added a solution of FcCOOH (0.2 mmol, 46 mg) in CH_2Cl_2 (25 ml). The solution was dried in air at room temperature. The resulting mass was dissolved in a mixture of CH_2Cl_2 and diethyl ether and left to crystallize with slow evaporation. Crystals suitable for XRD were formed a day later.

Oxidation of 1,2-diphenylacetylene. The catalyst (0.02 mmol) and 1,2-diphenylacetylene (0.2 mmol) were dissolved in DMSO (1 ml) in a ~10 ml glass tube. The tube was closed, and the reaction mixture was heated in an oil bath at 95 °C without stirring for the specified time (TLC monitoring, toluene/heptane, 1:1). The product R_f values were compared with those of authentic 1,2-diphenyl-ethane-1,2-dione (benzil) **5**. The crude material was purified by silica gel column chromatography using 1:1 toluene/heptane. The fractions containing products **5-7** were evaporated to dryness. The products were recrystallized from heptane at room temperature. The formed precipitates were collected and air-dried.

Table S1. Crystal Data and Structure Refinement for **1-4** and **7**.

Identification code	**1**	**2**	**3**	**4**	**7**
CCDC No	2158137	2158138	2158139	2158140	2158141
Empirical formula	$C_{18}H_{24}N_2O_4Pd$	$C_{18}H_{24}N_2O_4Pd$	$C_{36}H_{36}Fe_2N_2O_4Pd$	$C_{36}H_{36}Fe_2N_2O_4Pd$	$C_{28}H_{18}$
Formula weight	438.79	438.79	778.77	778.77	354.42
Temperature, K	100(2)	100(2)	100(2)	100(2)	150(2)
Crystal size, mm	0.33 × 0.25 × 0.18	0.21 × 0.15 × 0.10	0.24 × 0.23 × 0.05	0.060 × 0.040 × 0.020	0.080 × 0.040 × 0.020
Wavelength, Å	0.71073	0.71073	0.71073	0.74500	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/n$	*P*-1	*C*2/*c*
a, Å	8.367(2)	7.2081(2)	9.8707(2)	5.9190(17)	23.126(5)
b, Å	8.394(3)	7.6808(2)	11.0262(2)	8.7586(11)	4.8853(9)
c, Å	8.473(3)	9.2124(3)	14.3690(4)	15.725(5)	18.788(4)
α, deg.	89.949(8)	75.916(1)	90	105.717(3)	90
β, deg.	61.222(7)	67.741(1)	100.8298(11)	94.526(15)	122.597(7)
γ, deg.	63.451(7)	85.735(1)	90	97.137(7)	90
V, Å^3	448.8(2)	457.75(2)	1536.02(6)	773.2(3)	1788.3(7)
Z	1	1	2	1	4
Density (calc.), Mg/m^3	1.623	1.592	1.684	1.672	1.316
μ, mm^{-1}	1.059	1.038	1.555	1.743	0.075
F(000)	224	224	792	396	744
Theta range, deg.	2.820 – 30.701	3.054 – 30.657	2.314 – 30.604	1.420 – 27.090	2.091 – 25.059
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 12$, $-12 \le l \le 12$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-13 \le l \le 13$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-20 \le l \le 20$	$-7 \le h \le 7$, $-10 \le k \le 10$, $-19 \le l \le 19$	$-26 \le h \le 27$, $-5 \le k \le 5$, $-22 \le l \le 17$
Reflections collected	6813	7762	25123	11606	4925
Independent reflections	2752 (R_{int} = 0.0170)	2816 (R_{int} = 0.0204)	4733 (R_{int} = 0.0286)	2959 (R_{int} = 0.1010)	1567 (R_{int} = 0.1149)
Reflections observed	2744	2802	4362	2051	669
Data / restraints / parameters	2752 / 0 / 118	2816 / 0 / 118	4733 / 0 / 207	2959 / 0 / 207	1567 / 0 / 164
R_1 / wR_2 ($I > 2\sigma(I)$)	0.0156 / 0.0414	0.0172 / 0.0423	0.0257 / 0.0668	0.0563 / 0.1331	0.0698 / 0.1288
R_1 / wR_2 (all data)	0.0157 / 0.0415	0.0174 / 0.0424	0.0288 / 0.0686	0.0931/ 0.1527	0.1959 / 0.1685
Goodness-of-fit on F^2	1.136	1.110	1.078	1.018	0.930
Extinction coefficient	-	-	-	-	0.0075(14)
T_{min} / T_{max}	0.5799 / 0.6478	0.6866 / 0.7461	0.6619 / 0.7461	0.001 / 1.000	0.4742 / 0.5621
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å^{-3}	0.549 / -0.664	0.457 / -0.676	0.573 / -0.990	1.010 / -0.955	0.237 / -0.259

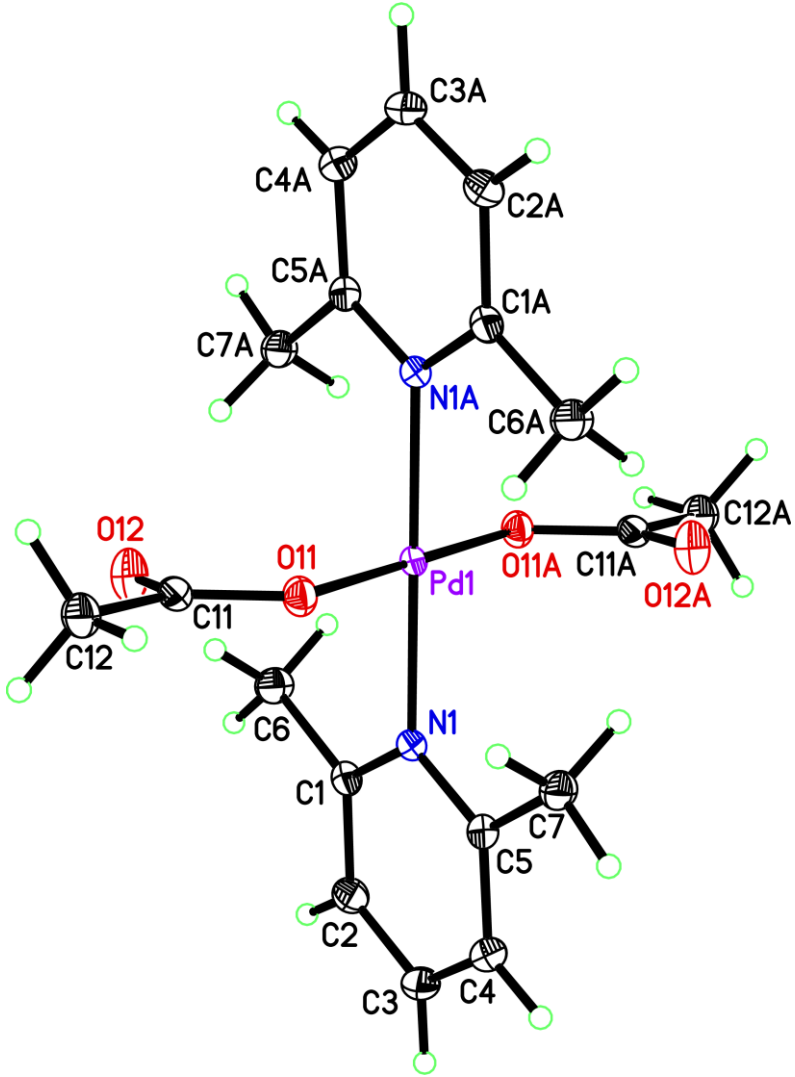

Figure S1. Molecular structure of square-planar complex **1** $[Pd(2,6\text{-lut})_2(OOCMe)_2]$. Atomic displacement parameters are shown at 50% probability level. Main geometrical parameters: Pd1-O11 2.0247(10) Å, Pd1-N1 2.0482(11) Å; O11-Pd1-$O11^{\#1}$ 180.00(6)°, O11-Pd1-$N1^{\#1}$ 88.44(4)°, $O11^{\#1}$-Pd1-$N1^{\#1}$ 91.56(4)°, O11-Pd1-N1 91.56(4)°, $O11^{\#1}$-Pd1-N1 88.44(4)°, $N1^{\#1}$-Pd1-N1 180.0°

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1,-y+1,-z

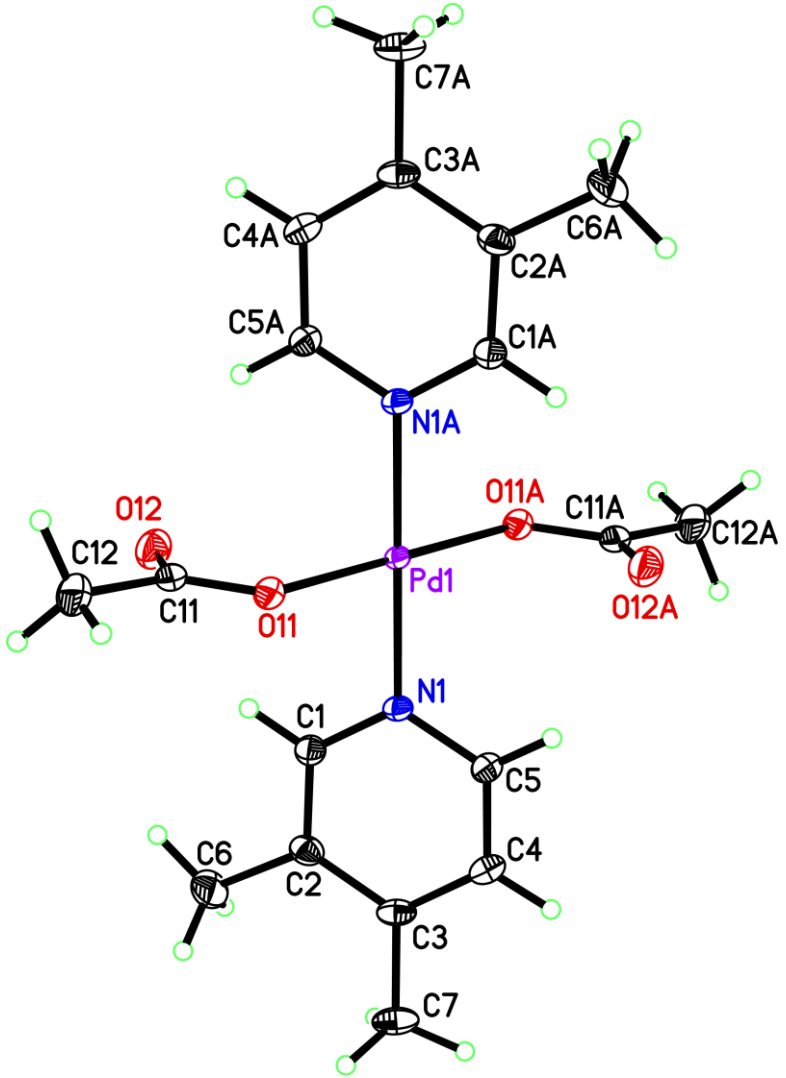

Figure S2. Molecular structure of square-planar complex **2** $[Pd(3,4\text{-lut})_2(OOCMe)_2]$. Atomic displacement parameters are shown at 50% probability level. Main geometrical parameters: Pd1-O11 2.0149(9) Å, Pd1-N1 2.0233(10) Å; O11-Pd1-$O11^{\#1}$ 180.00(5)°, O11-Pd1-N1 91.07(4)°, $O11^{\#1}$-Pd1-N1 88.93(4)°, O11-Pd1-$N1^{\#1}$ 88.93(4)°, $O11^{\#1}$-Pd1-$N1^{\#1}$ 91.07(4)°, N1-Pd1-$N1^{\#1}$ 180.0°.

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1,-y+1,-z+1

IR spectra of compounds 1-5

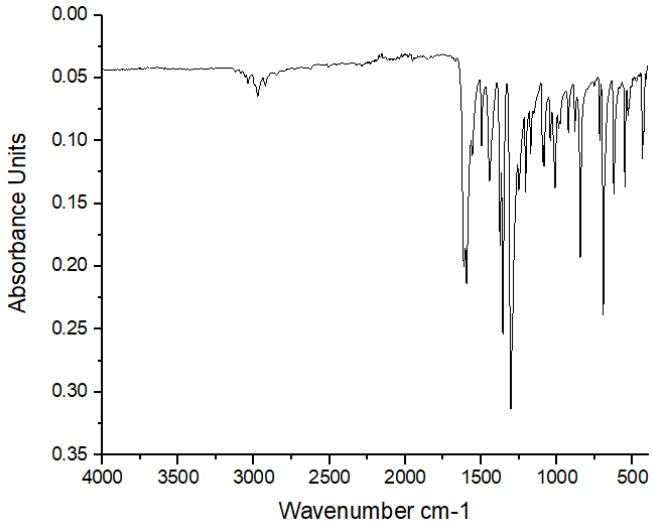

Figure S3 *Complex* $[Pd(2,6\text{-lut})_2(OAc)_2]$ **1**: green-yellow solid, yield 0.34 g (88 % based on Pd). IR (ATR, ν/cm^{-1}): 3054 (w), 2996 (w), 2926 (w), 2851 (w), 1596 (s), 1471 (m), 1435 (m), 1402 (w), 1357 (s), 1307 (vs), 1171 (m), 1117 (w), 1046 (m), 1014 (m), 926 (w), 781 (s), 733 (w), 689 (vs), 624 (w), 525 (w), 460 (w). Found (%): C, 49.80; H, 5.72, N 6.04. Calc. for $C_{18}H_{24}N_2O_4Pd$ (%): C, 49.27; H, 5.51; N, 6.38.

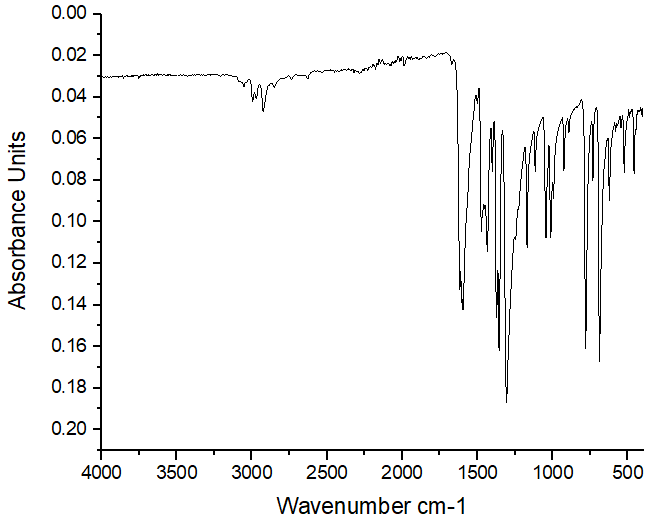

Figure S4 *Complex* $[Pd(3,4\text{-lut})_2(OAc)_2]$ **2**: light yellow solid, yield 0.21 g (55 % based on Pd). IR (ATR, ν/cm^{-1}): 2976 (w), 2924 (w), 1614 (s), 1596 (s), 1558 (m), 1498 (m), 1443 (m), 1375 (s), 1357 (vs), 1305 (vs), 1252 (w), 1207 (m), 1172 (w), 1085 (m), 1043 (w), 1012 (m), 924 (w), 882 (w), 846 (s), 718 (w), 694 (vs), 624 (m), 552 (m), 435 (m). Found (%): C, 49.55; H, 5.32, N 5.98. Calc. for $C_{18}H_{24}N_2O_4Pd$ (%): C, 49.27; H, 5.51; N, 6.38.

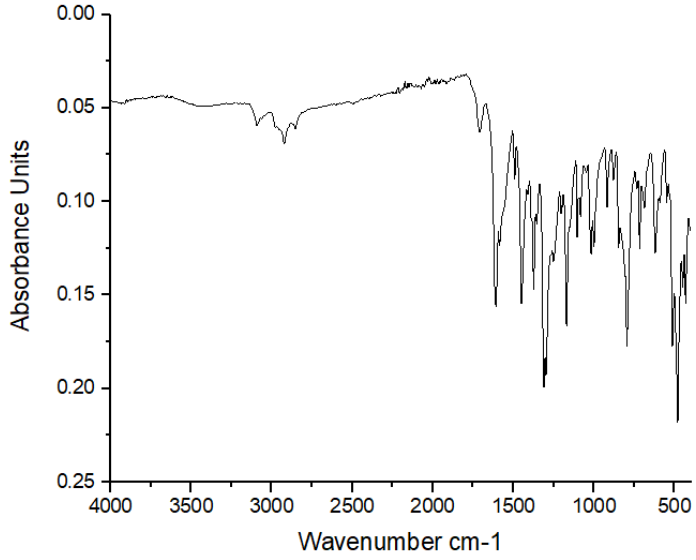

Figure S5 *Complex* [Pd(2,6-lut)$_2$(FcCOO)$_2$] **3**. Yield 72.2 mg (93 % based on Pd). IR (ATR, ν/cm^{-1}): 2925 (w), 1717 (w), 1597 (s), 1473 (m), 1450 (s), 1375 (m), 1309 (vs), 1175 (m), 1106 (m), 1046 (w), 1000 (m), 919 (w), 783 (s), 733 (m), 688 (m), 624 (w), 520 (s), 482 (s), 450 (m). Found (%): C, 54.95; H, 4.36; N, 3.24. Calc. for $C_{36}H_{36}Fe_2N_2O_4Pd$ (%): C, 55.52; H, 4.66; N, 3.60.

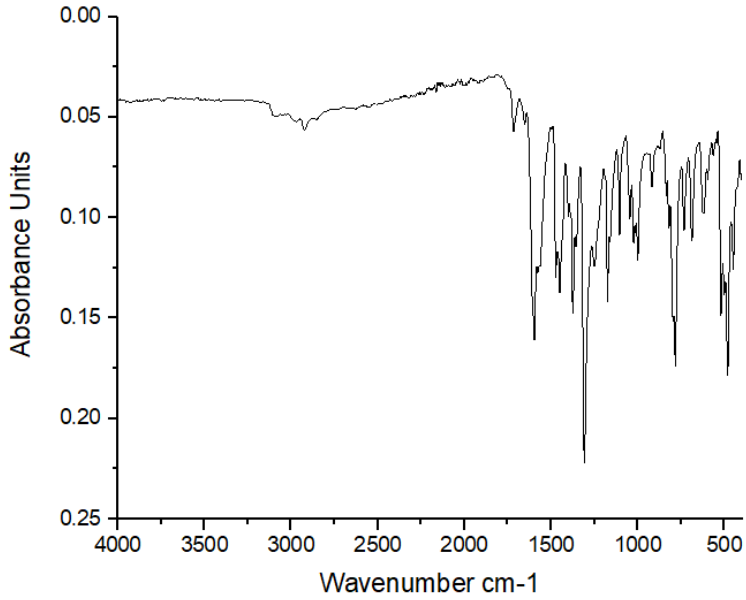

Figure S6 *Complex* [Pd(3,4-lut)$_2$(FcCOO)$_2$] **4**: Yield 72,9 mg (91 % based on Pd). IR (ATR, ν/cm^{-1}): 3092 (w), 2923 (w), 2853 (w), 1709 (w), 1609 (s), 1492 (w), 1452 (s), 1374 (m), 1311 (vs), 1171 (s), 1105 (w), 1083 (w), 1018 (m), 1000 (m), 919 (w), 796 (s), 733 (m), 620 (m), 513 (s), 481 (vs), 431 (m). Found (%): C, 55.18; H, 4.53; N, 3.45. Calc. for $C_{36}H_{36}Fe_2N_2O_4Pd$ (%): C, 55.52; H, 4.66; N, 3.60.

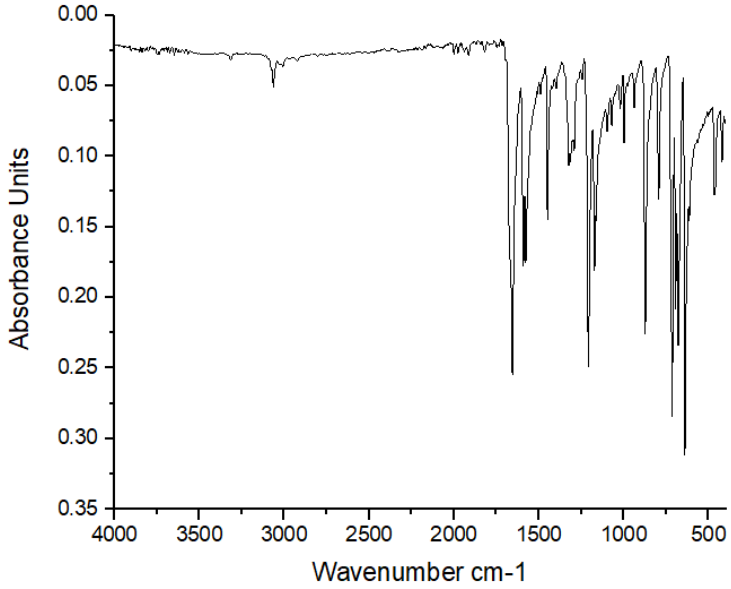

Figure S7 *1,2-Diphenylethane-1,2-dione (benzil)* **5** IR (ν^{-1}, ATR): 3060 (vw, br), 1670 (m), 1596 (w), 1449 (w), 1324 (v.w), 1265 (w), 1210 (m), 1175 (w), 1098 (v.w), 1072 (v.w), 1024 (vw), 1000 (vw), 936 (vw), 872 (w), 792 (vw), 733 (v.s, w), 717 (v.w), 701 (v.w), 684 (w), 642 (v.s), 615 (v.w) , 466 (vw).

Table S2 Solubility of $[Pd(L)_2(FcCOO)_2]$ bimetallic complexes in common solvents

Solvent	$[Pd(3,4\text{-lut})_2(FcCOO)_2]$ **4**	$[Pd(2,6\text{-lut})_2(FcCOO)_2]$ **3**	$[Pd(py)_2(FcCOO)_2]$
acetone	+/–	+/–	–
toluene	–	+/–	–
dichloromethane	+	+	–
DMSO	+	+	–
methanol	+/–	+/–	–