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Profound Steric Control of Reactivity in Aryl Halide Addition to Bis-Phosphine Palladium[0] Complexes [**]

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$P(tBu)(Cx)_2$ (1)

To a solution of 5.0 ml of *ter*butyllithium (1.7M in pentane, 8.6 mmol, Aldrich) in 25 ml of diethyl ether cooled at –78°C was slowly added 1.0 g (4.3 mmol) of dicyclohexylchlorophosphine (Strem). The solution was then slowly allowed to reach room temperature and stirred overnight. After filtration, 10 ml of degassed water were added, and the organic layer transferred to a Schlenk tube containing magnesium sulfate. After filtration and removal of the ether, the phosphine was obtained as a colorless liquid (0.71g, 65%).

^1H (δ, C_6D_6): 2.05 - 1.19 (m, 22H, Cx); 1.26 (d, 9H, 10.3 Hz, tBu).

^{13}C (δ, C_6D_6): 34.0 (d, 23 Hz, CH Cx); 33.3 (d, 16 Hz, CH_2 Cx); 31.7 (d, 10 Hz, CH_2 Cx); 30.9 (d, 13 Hz, CH_3 tBu); 30.2 (d, 21 Hz, C tBu); 28.4 (d, 16 Hz, CH_2 Cx); 28.3 (d, 13 Hz, CH_2 Cx); 27.1 (s, CH_2 Cx).

^{31}P (δ, C_6D_6): 28.2 (s)

HRMS (m / z) (as the oxide) : 271.219079 (calc : 271.219852).

$Pd[P(tBuCx_2)]_2$ (3)

In the glove box were introduced in a Schlenk tube 0.212g (1.00 mmol) of complex CpPd(allyl) and 0.584g (2.3 mmol) of *ter*butyldicyclohexylphosphine. 10 ml of toluene were then added and the red solution was heated for 2.5 hours at 75°C. After being allowed to cool down, the solvent was removed and the brown solid washed twice with methanol (2 * 7ml) to give a white solid. After recristallisation from toluene / methanol, 350 mg of microcrystals were obtained (57%).

^1H (δ, C_6D_6): 2.44 - 1.38 (m, 44H, Cx); 1.51 (t, 9H, $^3J_{PH} + ^5J_{PH} =$ 11.7 Hz)

^{13}C (δ, C_6D_6): 36.0 (t, $^3J_{PH}$ + $^5J_{PH}$ = 8 Hz, CH Cx); 33.9 (t, $^3J_{PH}$ + $^5J_{PH}$ = 10 Hz, CH_2 Cx); 33.1 (t, $^3J_{PH}$ + $^5J_{PH}$ = 9 Hz, C, tBu); 32.2 (t, $^3J_{PH}$ + $^5J_{PH}$ = 6 Hz, CH_2 Cx); 31.7 (t, $^3J_{PH}$ + $^5J_{PH}$ = 10 Hz, CH_2 Cx); 28.3 (t, $^3J_{PH}$ + $^5J_{PH}$ = 11 Hz, CH_2 Cx); 28.2 (t, $^3J_{PH}$ + $^5J_{PH}$ = 10 Hz, CH_2 Cx); 27.2 (s, CH_2 tBu).

^{31}P (δ, C_6D_6): 55.4 (s)

HRMS (m / z):(Calc for C32 H62 P2 Pd(106)614.3362); Found 614.3365

P(*t*Bu)$_2$Cx (2)

To a solution of 25.0 ml of *ter*buthyllithium (1.7M in pentane, 40 mmol, Aldrich) in 50 ml of diethylether cooled at –78°C were slowly added 1.60 ml (10 mmol) of cyclohexyldichlorophosphine.[5] The solution was then kept at this temperature for 7 hours then slowly allowed to reach room temperature and stirred overnight. After filtration, 10 ml of degassed water were added, and the organic layer transferred to a schlenk tube containing magnesium sulfate. After filtration and removal of the ether, the crude phosphine was obtained as a slightly yellow liquid which was then distilled under reduced pressure to give the pure phosphine as a colorless liquid (1.22 g, 53%).

^{1}H (δ, C_6D_6): 2.23 - 1.19 (m, 11H, Cx); 1.32 (d, 18H, 10.5 Hz, tBu).

^{13}C (δ, C_6D_6): 37.1 (d, 28.8 Hz, CH Cx); 34.1 (d, 14 Hz, CH_2 Cx); 33.0 (d, 27 Hz, C tBu); 31.4 (d, 14 Hz, CH_3 tBu); 29.3 (d, 9 Hz, CH_2 Cx); 27.1 (s, CH_2 Cx).

^{31}P (δ, C_6D_6): 49.2 (s)

HRMS (m / z) (as the oxide) : 245.203676 (calc : 245.203429).

Pd[P(*t*Bu$_2$Cx)]$_2$ (4)

In the glove box were introduced in a Schlenk tube 0.212g (1.00 mmol) of complex CpPd(allyl) and 0.563g (2.3 mmol) of di-*ter*butylcyclohexylphosphine. 10 ml of toluene were then added and the red solution was heated for 2.5 hours at 75°C. After being allowed to cool down, the solvent was removed and the brown solid washed twice with methanol (2 * 5 ml) to give a white solid. After recristallisation from toluene / methanol, 330 mg of microcrystals were obtained (55%).

^{1}H (δ, C_6D_6): 2.70 (m, 4H, Cx); 1.75 (m, 6H, Cx); 1.62 (m, 6H, Cx); 1.48 (t, 36H, $^3J_{PH} + {}^5J_{PH}$ = 11.5 Hz); 1.17 (m, 6H, Cx).

^{13}C (δ, C_6D_6): 39.7 (s, CH Cx); 35.9 (s, C, tBu); 35.2 (s, CH_2, Cx); 32.1 (t, $^3J_{PH} + {}^5J_{PH}$ = 10 Hz, CH_3 tBu); 29.2 (s, CH_2, Cx); 27.16 (s, CH_2, Cx).

^{31}P (δ, C_6D_6): 73.3 (s)

HRMS (m / z):(calc. for C28 H58 P2 Pd(106) 562.3049; Found 562.3049

Products from oxidative addition reactions :

9a ^{1}H NMR (250 MHz, C_6D_6) δ = 1.25 – 2.09 (m, 44H, Cx); 1.69 (t, 18H, $^3J + {}^5J$ = 12.4 Hz, tBu); 6.93 - 7.05 (m, 3H, Ar); 7.69 (m, 2H, Ar). ^{31}P NMR (101 MHz, C_6D_6) δ = 32.6 (br).

10 ^{1}H NMR (250 MHz, C_6D_6) δ = 0.97 – 1.92 (m, 11H, Cx); 1.45 (d, 18H, 12.6 Hz, tBu); 6.90 (t, 1H, 7.2 Hz, Ar); 7.07 (t, 2H, 7.8 Hz, Ar); 7.86 (d, 2H, 7.8 Hz, Ar). ^{31}P NMR (101 MHz, C_6D_6) δ = 64.4 (s).

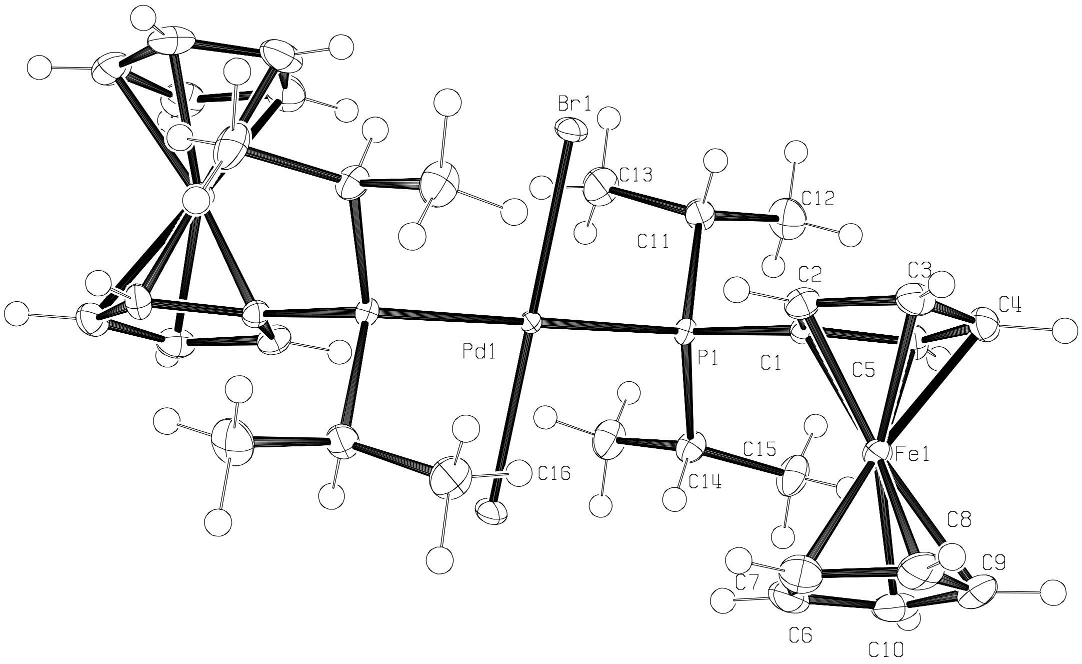
12 ^{1}H NMR (250 MHz, C_6D_6) δ = 1.09 (d, 27H, 12.5 Hz, tBu); 6.87 (m, 3H, Ph); 7.47 (m, 2H, Ph). ^{31}P NMR (101 MHz, C_6D_6) δ = 57.9 (s).

Supplementary data file for Angewandte Chemie Z18197

X-ray crystal structure for compound 15

$C_{32}H_{46}Br_2Fe_2P_2Pd$, M_r = 870.56, monoclinic, space group $P\ 2_1/a$, a (Å) = 9.4027(1), b (Å)=19.1503(3), c (Å)=9.6947(1), α (°)=90, β (°)=113.2419(7), • (°)=90, cell volume (Å^3)=1604.0, Z=2, R=0.0167.

Molecular structure of **15**. The hydrogen atoms on the peripheral ligands are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)-P(1) 2.3648(4), Pd(1)-Br(1) 2.43408(15); Br(1)-Pd(1)-P(1) 88.07(1).



Labels shown for one asymmetric unit only

A single crystal having dimensions approximately 0.24 x 0.24 x 0.42 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package[1].

Examination of the systematic absences of the intensity data showed the space group to be *P* $2_1/a$. The structure was solved using the direct-methods program SIR92[2], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite[3]. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0193, wR = 0.0167.

Attached is a thermal ellipsoid plot (ORTEP-3[4]) at 40% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

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4 ORTEP-3 v. 1.0.2, C. K. Johnson and M. K. Burnett, 1998.