Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 482–484

Cyclopentadienyl rhodium(III) complexes as catalysts for the insertion of phenyldiazoacetate into E−H bonds

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General information

The reactions were carried out in CH_2Cl_2, $CHCl_3$, or $CDCl_3$ which were dried over CaH_2. Complexes $[(C_5Me_5)CoI_2]_2$,[S1] $[(C_5Me_5)RhCl_2]_2$,[S2] $[(C_5Me_5)IrCl_2]_2$,[S2] $[(C_5H_5)RhI_2]_2$,[S3] $[(C_5Me_5)RhI_2]_2$,[S4] and $[(C_5H_2{}^tBu_2CH_2{}^tBu)RhI_2]_2$ (Ref. S5) were prepared according to the published procedures. Methyl (diazo)phenylacetate **1** was obtained according to the published procedure.[S6] All other reagents were obtained from commercial sources and used without purification. Macherey-Nagel silica gel 60 (230–400 mesh) was used for column chromatography, for thin layer chromatography (TLC) analysis Macherey-Nagel POLYGRAM SIL G/UV_{254} pre-coated polyester TLC plates (0.2 mm) were used. NMR spectra were measured on Bruker Avance 400 and Varian Inova 400 spectrometers. Chemical shifts are given in ppm relative to residual signal of $CHCl_3$ ($\delta_H \equiv 7.26$ ppm).

General experimental procedure: A 2 ml vial with Mininert valve was charged with methyl (diazo)phenylacetate **1** (0.2 mmol), E-H reagent (0.2 mmol) and $CDCl_3$ (0.5 ml). The solution was purged with argon for 3 min, the catalyst (2 mol%) was added, and the vial was sealed under inert atmosphere. The mixture was stirred at 20 °C first and then heated at 60 °C if no reaction was observed. The progress was monitored by the consumption of **1** (TLC). After 24 h, tetrachloroethylene standard (0.1 mmol) was added, and ^{1}H NMR spectrum was recorded to determine the yield of the product. For preparative purposes, the reaction was carried on 0.4 mmol scale with $[(C_5Me_5)RhI_2]_2$ catalyst and the isolation of products was carried out by column chromatography using EtOAc/petroleum ether mixtures as eluent.

(2-Methoxy-2-oxo-1-phenylethyl)borane, triethylamine complex 2a: 37% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, J = 7.3 Hz, 9H, Et_3N), 1.40 – 1.99 (br m, 2H, BH_2), 2.69 (m, 6H, Et_3N), 3.12 (m, 1H, CH), 3.59 (s, 3H, Me), 7.08 (m, 1H, Ph), 7.21 (t, J = 7.7 Hz, 2H, Ph), 7.44 (m, 2H, Ph). The spectrum is in accordance with the literature data.[S7]

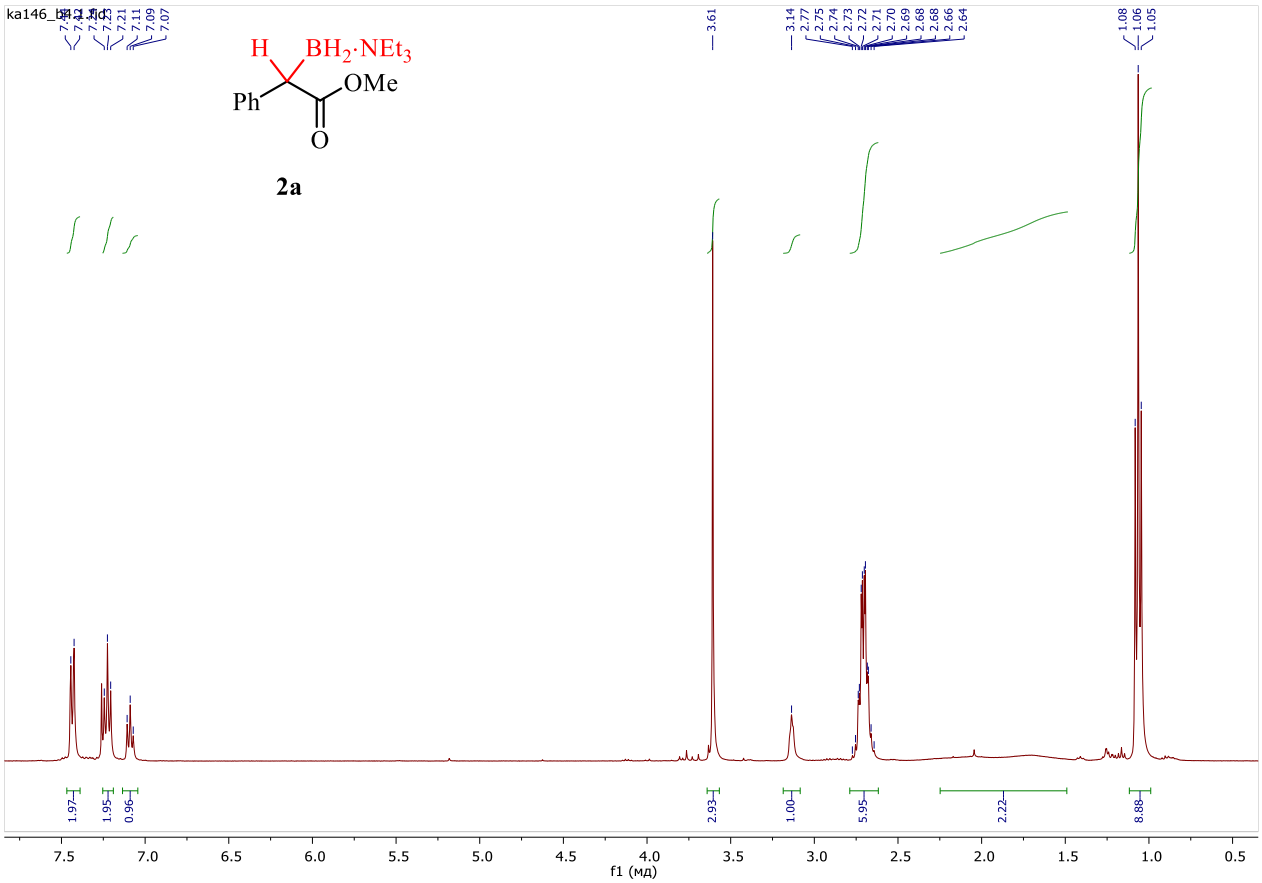
Methyl 2-phenyl-2-(triethylsilyl)acetate 2b: 61% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.59 (m appears as qd, J = 8.2, 3.5 Hz, 6H, Et_3Si), 0.91 (t, J = 7.9 Hz, 9H, Et_3Si), 3.53 (s, 1H, CH), 3.68 (s, 3H, Me), 7.17 (t, J = 7.3 Hz, 1H, Ph), 7.28 (t, J = 7.3 Hz, 2H, Ph), 7.36 (d, J = 6.9 Hz 2H, Ph). The spectrum is in accordance with the literature data.[S7]

Methyl 2-morpholino-2-phenylacetate 2c: 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (m, 4H, $(CH_2)_2N$), 3.68 (s, 3H, Me), 3.73 (t, J = 4.7 Hz, 4H, $(CH_2)_2O$), 3.99 (br.s, 1H, CH), 7.33 (m, 3H, Ph), 7.43 (m, 2H, Ph). The spectrum is in accordance with the literature data.[S7]

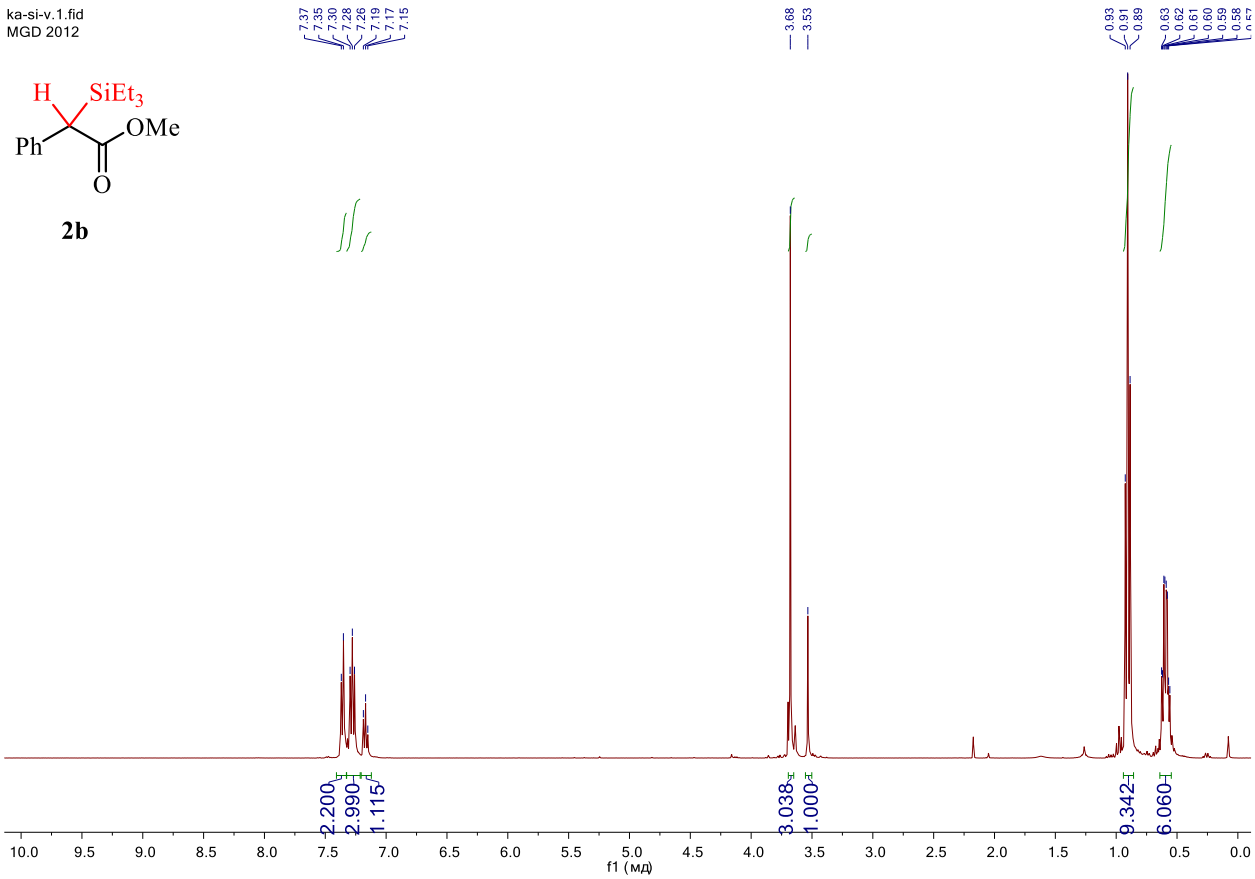
Methyl 2-benzamido-2-phenylacetate 2d: 84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75 (m, 3H, Me), 5.78 (d, 2H, J = 6.97 Hz, 1H, CH), 7.24 (bd, J = 6.9 Hz, 1H, NH), 7.30-7.55 (m, 8H, Ph), 7.83 (d, J = 7.0 Hz, 2H, Ph). The spectrum is in accordance with the literature data.[S8]

Dimethyl 2,5-diphenyl-3,4-diazahexa-2,4-dienedioate ("methyl benzoylformate azine") **3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.01 (s, 6H, Me), 7.40-7.56 (m, 6H, Ph), 7.78 (m, 4H, Ph). The spectrum is in accordance with the literature data.[S9] The identity of the compound was additionally confirmed by X-ray diffraction.

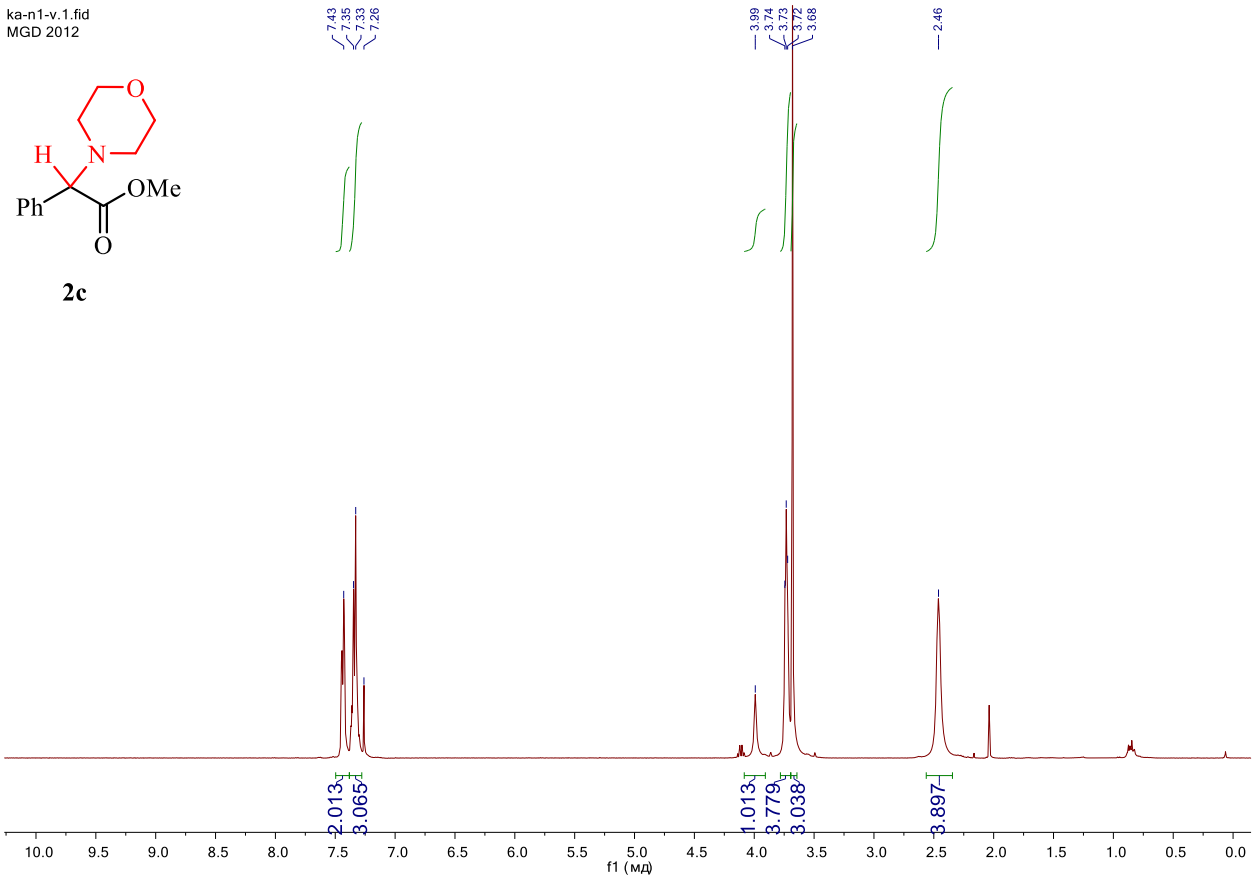
^{1}H NMR spectrum of **2a**



^{1}H NMR spectrum of **2b**

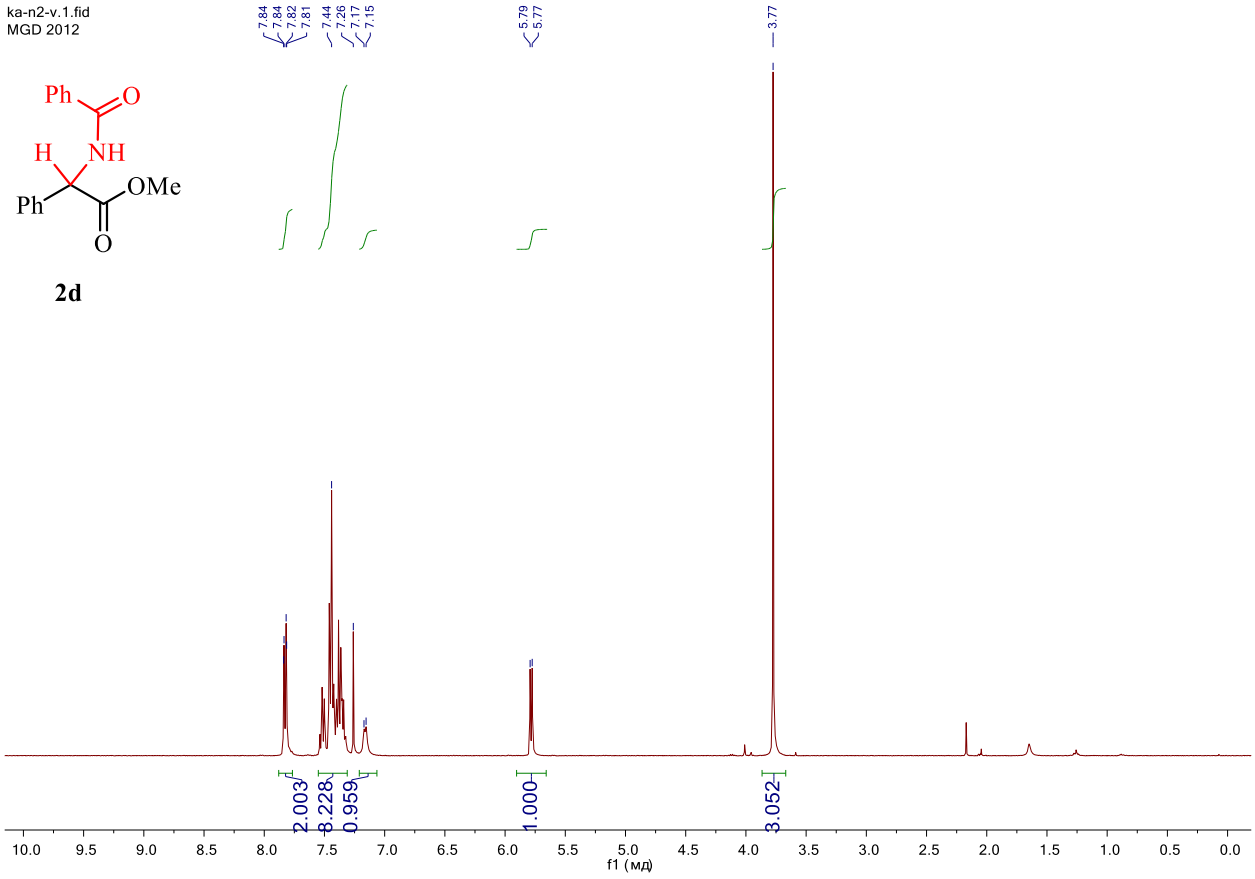


^{1}H NMR spectrum of **2c**



2c

^{1}H NMR spectrum of **2d**



2d

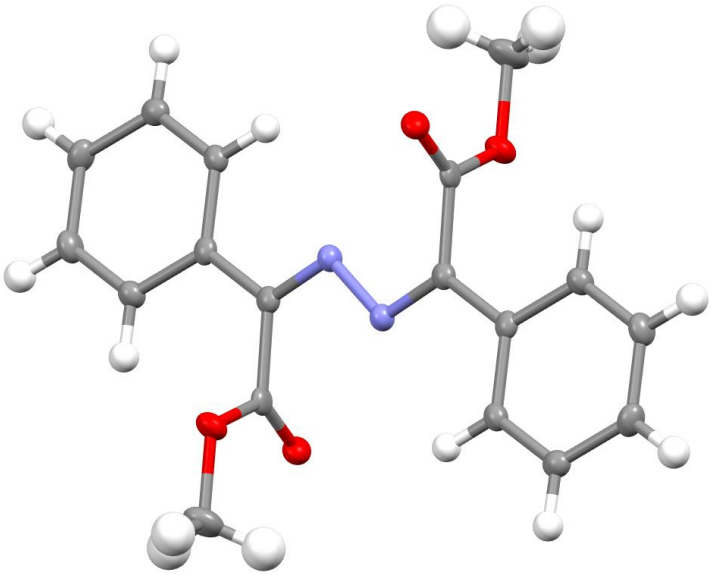


Figure S1 The structure of **3** as established by X-ray diffraction with atoms represented by thermal ellipsoids at 50% probability level. This structure has been established previously and deposited in Cambridge Crystallographic Data Centre (CCDC 2000393).[S10]

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