Supporting Information

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Expanding the family of mesoionic complexes: Donor properties and catalytic impact of palladated isoxazolylidenes

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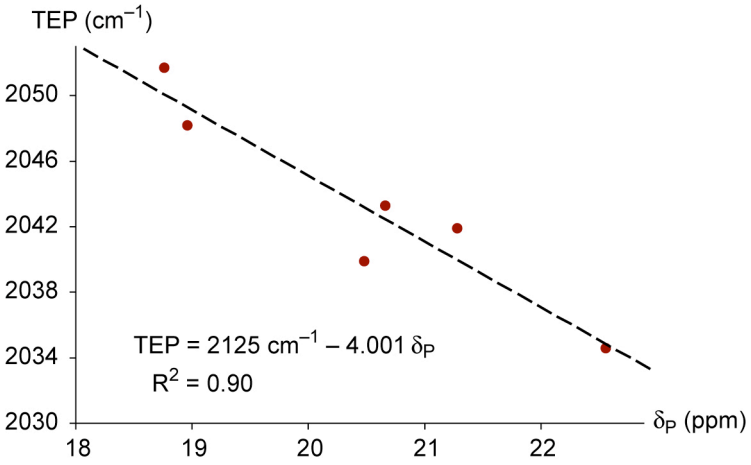
Content

Correlation of measured δ_P with calculated TEP



Synthetic procedures

General comments. All palladation reactions were performed using standard Schlenk techniques under an argon atmosphere unless stated otherwise. Toluene and CH_2Cl_2 were dried by passage through solvent purification columns. Complex **3**,[S1] and the iodo-azolium salts[S2] were prepared according to a previously reported procedure, all other reagents were commercially available and were used as received. All ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance spectrometers, chemical shifts (δ) are given in ppm and were referenced to residual solvent ^1H and ^{13}C resonances, and to external H_3PO_4, respectively (coupling constants J in Hz). Assignments are based either on distortionless enhancement of polarization transfer (DEPT) experiments or on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed by the Microanalytical Laboratory of the ETH Zurich (Switzerland).

4-Iodo-1,3,5-trimethylisoxazolium triflate (1a). Methyl trifluoromethanesulfonate (methyl triflate; 0.24 ml, 2.2 mmol) was added to a solution of 4-iodo-1,3,5-trimethylisoxazol in dry CH_2Cl_2 (5 mL) and the resulting mixture was stirred for 16 h at ambient temperature. The solvent

S1 Y. Han, H. V. Huyn and G. K. Tan, *Organometallics*, 2007, **26**, 6581.
S2 (a) H. B. Bensuan and M. S. R. Naidu, *Biochemistry*, 1967, **6**, 12; (b) M. Iglesias, M. Albrecht, *submitted.*

was evaporated under reduced pressure, and the remaining residue was redissolved in CH_2Cl_2 and precipitated with Et_2O. The residue was washed with Et_2O (3 × 10 mL), yielding **1a** as a white solid (630 mg, 81%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 4.29 (s, 3H, N–CH_3), 2.62, 2.58 (2 × s, 3H, C–CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.0, 162.8 (2 × C–Me), 121.0 ($^1J_{CF}$ = 353.7 Hz, CF_3), 67.2 (C–I), 40.3 (N–CH_3), 14.5, 13.8 (2 × C–*C*H_3). Anal. Calcd. for $C_7H_9F_3INO_4S$ (387.12): C, 21.95; H, 2.34; N, 3.62. Found: C, 21.95; H, 2.25; N, 3.58.

4-Iodo-1,3,5-trimethylisoxazolium BF_4 (1b).

Trimethyloxonium tetrafluoroborate (75 mg, 0.50 mmol) was added to a solution of 4-iodo-3,5-dimethylisoxazole (110 mg, 0.50 mmol) in dry CH_2Cl_2 (3 mL) and the resulting mixture was stirred for 16 h at ambient temperature. The solvent was evaporated under reduced pressure, and the remaining residue was redissolved in CH_2Cl_2 and precipitated with Et_2O. The residue was washed with Et_2O (3 × 5 mL), yielding **1b** as a white solid (130 mg, 85%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 4.38 (s, 3H, N–CH_3), 2.71, 2.68 (2 × s, 3H, C–CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.4, 162.6 (2 × C–Me), 66.9 (C–I), 40.3 (N–CH_3), 13.7, 13.0 (2 × C–*C*H_3). Anal. Calcd. for $C_6H_{10}BF_4INO$ (324.85): C, 22.18; H, 2.79; N, 3.96. Found: C, 22.58; H, 2.78; N, 3.96.

***Trans*-(1,3,5-trimethylisoxazolin-4-ylidene)iodobis(triphenylphosphine)palladium(II) BF_4 (2b).**

Solid $Pd(PPh_3)_4$ (144 mg, 0.125 mmol) and 4-iodo-1,3,5-trimethylisoxazolium tretrafluoroborate **1b** (40 mg, 0.125 mmol) were dissolved in dry toluene (10 mL). After stirring for 16 h at ambient temperature, the resulting pale orange suspension was concentrated to dryness. The precipitate was redissolved in CH_2Cl_2 (3 mL) and precipitated with Et_2O (3 × 10 mL), subsequently washed with copious amounts of Et_2O until the filtrate was colourless and dried under vacuum to afford **2b** as a pale yellow solid (100 mg, 84%). ^{1}H NMR (360 MHz, CD_2Cl_2): δ 7.66 – 7.40 (m, 30H, H_{ar}), 3.88 (s, 3H, N–CH_3), 2.06, 1.76 (2 × s, 3H, C–CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 167.9 ($^2J_{CP}$ = 3.8 Hz, C–Pd), 162.6 (C–Me), 134.2 ($^2J_{CP}$ = 6.2 Hz, C_{ar}), 131.4 (C_{ar}), 129.2 ($^1J_{CP}$ = 25.1 Hz, C_{ar}), 128.8 ($^3J_{CP}$ = 5.2 Hz, C_{ar}), 39.6 (N–CH_3), 15.2, 13.7 (2 × C–*C*H_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 23.5 (PPh_3). Anal. Calcd. for $C_{42}H_{39}BF_4INOP_2Pd$ (955.84): C, 52.78; H, 4.11; N, 1.47. Found: C, 52.44; H, 4.27; N, 1.51.

General procedure for the preparation of the palladium complexes 4–7. Solid $Pd(PPh_3)_4$ and the azolium triflate (1 molequiv.) were dissolved in dry CH_2Cl_2 and stirred for 16 h at ambient temperature. After concentrating the pale orange solution to 3 mL, the product precipitated by addition of Et_2O (10 mL). The precipitate was redissolved into CH_2Cl_2 (3 mL) and precipitated with Et_2O (3×), and subsequently washed with Et_2O until the filtrate was colourless. The residue was then dried in vacuo.

***Trans*-(1,3-dimethylimidazolin-4-ylidene)iodobis(triphenylphosphine)palladium(II) triflate (4).** Starting from $Pd(PPh_3)_4$ (288 mg, 0.25 mmol) and 4-iodo-1,3-dimethylimidazolium triflate (105 mg, 0.25 mmol) in CH_2Cl_2 (20 mL). Yield for **4**: 180 mg (72%). ^{1}H NMR (360 MHz, CD_2Cl_2): δ 8.17 (s, 1H, NCHN), 7.62–7.45 (m, 30H, H_{ar}), 5.70 (s, 1H, H_{imi}), 3.31, 3.24 (2 × s, 3H, N–CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 145.7 ($^2J_{CP}$ = 7.1, C–Pd), 136.7 (NCHN), 134.8 ($^2J_{CP}$ = 4.9, C_{ar}), 131.5 (C_{ar}), 131.0 ($^1J_{CP}$ = 20.1, C_{ar}), 128.8 ($^3J_{CP}$ = 4.1, C_{ar}), 123.3 ($^3J_{CP}$ = 3.8, C_{imi}–H), 122.53 ($^1J_{CF}$ = 255.1 Hz, CF_3), 38.0, 35.7 (2 × N–CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 20.66 (PPh_3). Anal. Calcd. for $C_{42}H_{38}F_3IN_2O_3P_2PdS$ (1003.09) × Et_2O: C, 51.29; H, 4.49; N, 2.60. Found: C, 51.39; H, 4.12; N, 2.91.

***Trans*-(1,2,3,5-tetramethylimidazolin-4-ylidene)iodobis(triphenylphosphine)palladium(II) triflate (5).** Starting from $Pd(PPh_3)_4$ (288 mg, 0.25 mmol) and 4-iodo-1,2,3,5-tetramethylimidazolium triflate (100 mg, 0.25 mmol) in CH_2Cl_2 (10 ml). Yield 175 mg (0.17 mmol, 68%). Analytically pure material was obtained by recrystallisation of **5** from CH_2Cl_2 /Et_2O. ^{1}H NMR (360 MHz, CD_2Cl_2): δ 7.60–7.40 (m, 30H, H_{ar}), 3.07, 3.03 (2 × s, 3H, N–CH_3), 1.96, 1.59 (2 × s, 3H, CCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 142.3 (NCN), 137.4 ($^2J_{CP}$ = 8.8, C–Pd), 134.5 ($^2J_{CP}$ = 6.1, C_{ar}), 131.2 (C_{ar}), 130.6 ($^1J_{CP}$ = 24.8, C_{ar}), 128.3 ($^3J_{CP}$ = 5.2, C_{ar}), 126.8 ($^3J_{CP}$ = 4.8, C_{imi}–Me), 121.0 ($^1J_{CF}$ = 270.0 Hz, CF_3), 36.6, 32.1 (2 × N–CH_3), 10.9, 10.3 (2 × C_{imi}–CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 20.48 (PPh_3). Anal. Calcd. for $C_{43}H_{40}F_3IN_2O_3P_2PdS$ (1031.15) × 0.5 CH_2Cl_2: C, 49.69; H, 4.22; N, 2.60. Found: C, 49.23; H, 3.90; N, 2.58.

***Trans*-(1,3-dimethylpyridin-2-ylidene)iodobis(triphenylphosphine)palladium(II) triflate (6).** Starting from $Pd(PPh_3)_4$ (288 mg, 0.25 mmol) and 2-iodo-1,3-dimethylpyridinium triflate (94 mg,

0.25 mmol) in CH_2Cl_2 (20 mL). Yield 192 mg (0.19 mmol, 76%). ^{1}H NMR (360 MHz, CD_2Cl_2): δ 7.88 (d, $^3J_{HH}$ = 5.9 Hz, 1H, H_{py}), 7.58–7.43 (m, 30H, H_{ar}), 6.97–6.89 (m, 2H, H_{py}), 4.13 (s, 3H, N–CH_3), 2.44 (s, 3H, C–CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 193.7 ($^2J_{CP}$ = 4.9 Hz, C–Pd), 144.9 ($^2J_{CP}$ = 2.2 Hz, C_{py}), 143.0 (C_{py}), 138.5 (C_{py}), 134.8 (broad, C_{ar}), 132.0 (C_{ar}), 130.5 ($^1J_{CP}$ = 25.2 Hz, C_{ar}), 129.2 ($^3J_{CP}$ = 5.1 Hz, C_{ar}), 123.3 (C_{py}–Me), 121.5 ($^1J_{CF}$ = 319.3 Hz, CF_3), 52.5 (N–CH_3), 24.6 (C_{py}–*C*H_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 18.96 (PPh_3). Anal. Calcd. for $C_{44}H_{39}F_3INO_3P_2PdS$ (1014.13): C, 52.11; H, 3.88; N, 1.38. Found: C, 52.18; H, 3.79; N, 1.40.

***Trans*-(1,3-dimethylimidazolin-2-ylidene)iodobis(triphenylphosphine)palladium(II) triflate (7).** Starting from $Pd(PPh_3)_4$ (288 mg, 0.25 mmol) and 2-iodo-1,3-dimethylimidazolium triflate (92 mg, 0.25 mmol) in CH_2Cl_2 (20 mL). Yield 162 mg (65%). ^{1}H NMR (360 MHz, DMSO–d_6): δ 7.60–7.45 (m, 30H, H_{ar}), 6.72 (s, 2H, H_{imi}), 3.26 (s, 6H, N–CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 162.3 ($^2J_{CP}$ = 8.4 Hz, C–Pd), 134.2 ($^2J_{CP}$ = 6.2 Hz, C_{ar}), 131.6 (C_{ar}), 130.1 ($^1J_{CP}$ = 25.7 Hz, C_{ar}), 128.9 ($^3J_{CP}$ = 5.2 Hz, C_{ar}), 124.7 (C_{imi}), 121.0 ($^1J_{CF}$ = 321.3 Hz, CF_3), 37.0 (N–CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 18.76 (PPh_3). Anal. Calcd. for $C_{42}H_{38}F_3IN_2O_3P_2PdS$ (1003.11): C, 50.29; H, 3.82; N, 2.79. Found: C, 50.23; H, 3.85; N, 2.77.

Structure determination and refinement of 2b

Suitable crystals of **2b** were obtained as yellow plates. The intensity data were collected at 173 K on a Stoe Mark II-Image Plate Diffraction System equipped with a two-circle goniometer and using MoKα graphite monochromated radiation (λ = 0.71073 Å). The mage plate distance was 130 mm. The structure was solved by direct methods using SHELXS-97[S3] and refined by full-matrix least-squares on F^2 with SHELXL-97.[S2] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. A semi-empirical absorption correction was applied using the MULscanABS routine in PLATON.[S4]

The crystal was a twin. As a result of the twin integration, 35% of reflections are overlapping and only 65% have been used for the structure refinement. Further details on data collection and refinement parameters are collected in Table S1. Crystallographic data (excluding structure

S3 G. M. Scheldrick, *Acta Crystallogr. A,* 2008, **64**, 112.
S4 A. L. Spek, *Acta Crystallogr. D,* 2009, **65**, 148.

factors) for structure **2b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC xxx. Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int.) +44-1223-336-033; E-mail: deposit@ccds.cam.ac.uk].

Table S1 Crystallographic data for complex **2b**.

crystal colour, shape	yellow plate
crystal size /mm	0.30 × 0.18 × 0.12
empirical formula	$C_{42}H_{41}BF_4INO_3P_2Pd$
Fw /g mol^{-1}	989.81
T /K	173(2)
crystal system	triclinic
space group	P–1 (No. 2)
unit cell dimensions	
a /Å	13.3917(9)
b /Å	15.7897(10)
c /Å	20.5894(15)
α /deg	92.386(6)
β /deg	99.693(6)
γ /deg	90.623(5)
V /Å^3	4287.1(5)
Z	4
D_{calc} /g cm^{-3}	1.534
μ /mm^{-1}	1.283
measured reflections	18577
independent reflections	9996
observed reflections [$I > 2\sigma$(I)]	7997
R_{int}	0.0708
transmission range	0.588 – 0.934
parameters restraints	974, 0
R_1,[a] wR_2[b]	0.1155, 0.3298
GOF	1.082
min/max residual density /e Å^{-3}	–1.071, 2.029

[a] $R_1 = \Sigma||F_O|-|F_C||/\Sigma|F_O|$ for all $I > 2\sigma(I)$ [b] $wR_2 = [\Sigma w(F_O^2-F_C^2)^2/\Sigma(w(F_O^4)]^{1/2}$