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Mesoionic oxides: facile access from triazolium salts or triazolylidene copper precursors and catalytic relevance

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Content

1. Synthetic procedures

General considerations

The syntheses of complexes **3** were carried out under an inert atmosphere of N_2 using Schlenk technique and dry solvents. All ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at room temperature on Varian spectrometers and chemical shift were referenced to $SiMe_4$ (δ in ppm, J in Hz). IR spectra were recorded on a Varian 3100 FT-IR spectrometer. Compounds **1** were synthesized according to literature procedures.[S1] All other reagents were purchased from commercial sources and were used as received. CsOH monohydrate containing 15-20% water was purchased from Fluka in ≥95% purity grade, or ≥99.9% from Alfa Aesar.[S2] Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin, Ireland, using a Exter Analytical CE-440 Elemental Analyzer.

Synthesis of 2a

Method A: Compound **1a** (300 mg, 1.00 mmol.) and $CsOH{\cdot}H_2O$ (336 mg, 2.0 mmol) were stirred in THF (20 mL) for 24 h. The mixture was filtered through Celite, the solvent removed and the crude was purified by chromatography (SiO_2; CH_2Cl_2/Et_2O 10:3). Yield: 26%.

Similar results were obtained when using lower quantities of CsOH. Stirring **1a** (45 mg, 0.12 mmol) and $CsOH{\cdot}H_2O$ (21 mg, 0.12 mmol, 1 molequiv) in THF for 24 h gave a crude mixture composed of **2a** (79%) and 1-methyl-4-phenyl triazole (15%, resulting from demethylation). Likewise, **2a** is formed from **1a** when reacting with Cs_2CO_3 (1 molequiv). This latter reaction is substantially faster in the presence of CuCl, (75% conversion after 14 h *vs* 42% conversion in the absence of CuCl).

Method B: Compound **3a** (200 mg, 0.60 mmol), and $CsOH{\cdot}H_2O$ (201 mg, 1.2 mmol) were stirred in THF (20 mL) for 24 h. The mixture was filtered through Celite and the solvent removed under vacuum. The solid was dissolved in CH_2Cl_2 and filtered through a short pad of SiO_2. The filtrate was concentrated and layered with Et_2O affording a white precipitate, which was isolated and dried. Yield: 70%.

IR ($CHCl_3$): ν(CO) 1644 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.12 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, $H_{ortho\ Ctrz}$), 7.69 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, $H_{ortho\ Ntrz}$), 7.50 (t, 4H, $^{3}J_{HH}$ = 7.7 Hz, H_{meta}), 7.38 (m, 2H, H_{para}), 4.12 (s, 3H, NCH_3).$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 155.6 (CO) 136.2 (C_{trz}–Ph), 129.1, 128.9 (2 × C_{meta}), 128.3, 126.8 (2 × C_{para}), 127.9 ($C_{ortho\ Ctrz}$), 127.7 (C_{ipso}), 121.1 ($C_{ortho\ Ntrz}$), 119.3 (C_{ipso}), 39.4 (NCH_3). Elem. anal. calcd. for $C_{15}H_{13}ON_3$

(251.11) × 1/3 H_2O: C, 70.02; H, 5.35; N, 16.33; found C, 70.25; H, 5.19; N, 16.05. HRMS (ESI) calcd. for $C_{15}H_{13}ON_3Na$ $[M+Na]^+$ 274.0956, found 274.0967.

Synthesis of 2b

To compound **3b** (90 mg, 0.19 mmol), a suspension of $CsOH·H_2O$ (62 mg, 0.37 mmol) in THF (20 mL) was added and the mixture stirred for 24 h. After that time, another 2 equiv. of $CsOH·H_2O$ were added and the mixture stirred for another 24 h. The solvent was removed under reduced pressure and the crude mixture was purified by chromatography (SiO_2; CH_2Cl_2/Et_2O 10:1). Yield 56 %.

IR ($CHCl_3$): ν(CO) 1643 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.44 (t, 1H, $^3J_{HH}$ = 7.5 Hz, H_{Ar*}), 7.28 (d, 2H, $^3J_{HH}$ = 7.5 Hz, H_{Ar*}), 6.98 (s, 2H, H_{Mes}), 3.74 (s, 3H, NCH_3), 2.73 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, $CHMe_2$), 2.31 (s, 3H, Mes–CH_3), 2.21 (s, 6H, Mes–CH_3), 1.26, 1.20 (2 × d, 6H, $^3J_{HH}$ = 6.9 Hz, CHMe–CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 156.5 (CO), 146.9 (C_{Ar*}–C), 139.7, 139.3 (2 × C_{Mes}–C), 134.6 (C_{Ar*}–C), 130.5 (C_{Ar*}–H), 128.7 (C_{Mes}–H), 123.8 (C_{Ar*}–H), 122.4 (C_{Mes}–C), 118.1 (C_{trz}–Ar*), 37.8 (NCH_3), 28.8 ($CHMe_2$), 23.6, 23.5 (2 × CHMe–CH_3), 21.2, 19.9 (2 × Mes–CH_3). HRMS (ESI) calcd. for $C_{24}H_{32}ON_3$ $[M+H]^+$ 378.2545, found 378.2562.

Synthesis of 2c

Method A: Compound **1c** (300 mg, 1.00 mmol.) and $CsOH·H_2O$ (336 mg, 2.0 mmol) were stirred in THF (20 mL) for 24 h. The mixture was filtered through Celite, the solvent removed and the crude was purified by chromatography (SiO_2; CH_2Cl_2/acetone 20:1). Yield: 32%.

Same results were obtained when performing the reaction at a 1:1 molar ratio of **1a** and CsOH. Thus, stirring **1c** (90 mg, 0.30 mmol) and $CsOH·H_2O$ (50 mg, 0.30 mmol) for 24 h gave a crude **2c** (88% conversion) along with minor quantities of the corresponding demethylated 1,4- and 1,5-triazole.

Method B: Compound **1c** (330 mg, 1.09 mmol.), Ag_2O (131 mg, 0.57 mmol.) and Me_4NCl (62 mg, 0.57 mmol) were stirred overnight under N_2 in CH_2Cl_2/MeCN (1:1, 20 mL). CuCl (108 mg, 1.09 mmol) was added and the mixture was stirred for another 6 h. The resulting mixture was filtered through Celite under N_2 and dried under vacuum. To the resulting solid, a suspension of $CsOH·H_2O$ (370 mg, 2.2 mmol) in THF was added and the mixture stirred for 24 h. The mixture was filtered through Celite, the solvent removed and the resulting solid was

dissolved in CH_2Cl_2 and layered with Et_2O affording a white precipitate, which was isolated and dried. Yield: 89%.

IR ($CHCl_3$): ν(CO) 1634 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.63 (d, 2H, $^3J_{HH}$ = 7.7 Hz, H_{ortho}), 7.46 (t, 2H, $^3J_{HH}$ = 7.7 Hz, H_{meta}), 7.35 (t, 1H, $^3J_{HH}$ = 7.7 Hz, H_{para}), 4.01, 3.73 (2 × s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ 156.0 (CO), 128.9 (C_{ortho}), 128.1 (C_{para}), 127.8 (C_{meta}), 127.1 (C_{ipso}), 118.4 (C_{trz}–Ph), 39.1, 31.2 (2 × NCH_3). Elem. anal. calcd. for $C_{10}H_{12}N_3O$ (190.1) × 1/2 H_2O: C, 60.59; H, 6.10; N, 21.20 found: C, 60.98; H, 5.76; N, 21.16. HRMS (ESI) calcd. for $C_{10}H_{12}N_3O$ $[M]^+$ 190.0980, found 190.0988.

Synthesis of 3b

Compound **1b** (200 mg, 0.41 mmol.), Ag_2O (47 mg, 0.21 mmol.) and Me_4NCl (20 mg, 0.21 mmol) were stirred overnight under N_2 in CH_2Cl_2/MeCN (1:1, 20 mL). CuCl (40 mg, 0.41 mmol) was added and the mixture was stirred for another 6 h. The resulting suspension was filtered through Celite, the filtrate was concentrated and layered with Et_2O to form a white precipitate, which was isolated and dried. Yield: 82%.

^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.52 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, H_{Ar*}), 7.31 (d, 2H, $^3J_{HH}$ = 7.8 Hz, H_{Ar*}), 7.02 (s, 2H, H_{Mes}), 3.88 (s, 3 H, NCH_3), 2.36 (m, 5H, Mes–CH_3 + Ar*–$CHMe_2$), 2.11 (s, 6H, Mes–CH_3),1.31 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CHMe–CH_3), 1.18 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CHMe–CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 146.9 (C_{trz}–Cu), 144.8 (C_{Ar*}–C), 140.6, 137.8 (2 × C_{Mes}–C), 135.9 (C_{Ar*}–C), 131.2 (C_{Ar*}–H), 129.1 (C_{Mes}–H), 124.1 (C_{Ar*}–H), 122.8 (C_{Mes}–C), 36.1 (NCH_3) 28.81 (Ar*–CH), 24.3 (CHMe–CH_3), 24.0 (CHMe–CH_3), 21.3, 20.2 (2 × C_{Mes}–CH_3). Elem. anal. calcd. for $C_{24}H_{31}N_3ClCu$ (459.15) × 1/2 H_2O: C, 61.39; H, 6.87; N, 8.95; found: C, 61.53; H, 6.71; N, 8.57. HRMS (ESI) calcd. for $C_{24}H_{31}N_3ClCuNa$ $[M+Na]^+$: 482.1406, found 482.1400.

Synthesis of 6a

Method A: Compound **4a** (60 mg, 0.21 mmol) and CsOH (140 mg, 0.84 mmol) were stirred for 24 h in THF (6 mL). The mixture was filtered through Celite and the solvent removed under vacuum to obtain a brown oil which was purified by chromatography (SiO_2; acetone). Yield 13 %

Method B: Compound **5a** (50 mg, 0.21 mmol) and CsOH (110 mg, 0.42 mmol mmol) were stirred for 24 h in THF (6 mL). The mixture was filtered trough Celite and the solvent

removed under vacuum to obtain a brown oil which was purified by chromatography (SiO_2; acetone). Yield 49 %

IR ($CHCl_3$): ν(CO) 1670 cm^{-1}.^{1}H NMR (400 MHz, CD_3CN, 30 °C) δ 8.51 (d, 1H, $^3J_{HH}$ = 4.8 Hz, H_{py}), 7.73 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, H_{py}), 7.25 (dd, 1H, $^3J_{HH}$ = 7.8 Hz,$^3J_{HH}$ = 4.8 Hz, H_{py}), 7.17 (d, 1H, $^3J_{HH}$ = 7.8 Hz, H_{py}), 6.44, 6.39 (2 × d, 1H, $^3J_{HH}$ = 3 Hz, H_{imid}), 4.84 (s, 2H, NCH_2-py), 4.30 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, $CHMe_2$), 1.28 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 30 °C) δ 155.8 (C_{Py}–imid), 151.3 (CO), 148.3, 136.0, 121.6, 121.2 (4 × C_{py}–H), 109.61, 106.0 (2 × C_{imid}–H), 47.8 (NCH_2), 43.7 ($NCHMe_2$) 21.1 (C–*C*H_3). HRMS (ESI) calcd. for $C_{12}H_{15}N_3O$ $[M+H]^+$ 218.1280, found 218.1283.

Synthesis of 6b

Method A: Compound **4b** (50 mg, 0.23 mmol) and CsOH (158 mg, 0.94 mmol) were stirred for 24 h in THF (6 mL). The mixture was filtered through celite and the solvent removed under vacuum to obtain an yellow oil which was purified by chromatography (SiO_2; CH_2Cl_2/acetone 1:1).Yield 37%.

Method B: Compound **5b** (50 mg, 0.21 mmol) and CsOH (140 mg, 0.84 mmol) were stirred for 24 h in THF (6 mL). The mixture was then filtered through Celite, the solvent removed under vacuum to obtain a yellow oil that was purified by chromatography (SiO_2; CH_2Cl_2/acetone 1:1). Yield 48%.

IR ($CHCl_3$): ν(CO) 1672 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 6.18, 6.16 (2 × d, 1H, $^3J_{HH}$ = 2.9 Hz, H_{imid}), 3.56 (t, 2H, $^3J_{HH}$ = 7.3 Hz, NCH_2), 3.25 (s, 3H, NCH_3), 1.68 (q, 2H, $^3J_{HH}$ = 7.3 Hz, C*H*$_2$CH$_3$), 0.94 (t, 3H, $^3J_{HH}$ = 7.3, CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 153.2 (CO), 114.1, 110.8 (2 × C_{imid}–H), 45.2 (NCH_2), 36.3 (NCH_3), 22.8 (*C*H_2CH$_3$), 11.03 (CH_2*C*H_3). HRMS (ESI) calcd. for $C_7H_{13}N_2O$ $[M+H]^+$ 141.1028, found: 141.1031.

2. IR spectroscopic data

Table S1 IR spectroscopy data of **2a** in different solvents [a]

solvent	ν_{CO} /cm^{-1}	ε_r	μ /D
$CHCl_3$	1634	4.89	1.02
Et_2O	1660	4.42	1.11
CH_2Cl_2	1640	9.02	1.60
$NCCH_3$	1641	35.94	3.95
KBr	1603	n.a.	n.a.

[a] relative permittivity (ε_r) and modulus of the molecular dipole moment (μ) from J.-L. Abboud and R. Notario, *Pure Appl. Chem*., 1999, **71**, 645–718.

While the IR stretch vibration does not correlate with the relative permittivity or the molecular dipole of the solvent, betaines alter their resonance contributions in dependence of solvent polarity; see for examples: R. Huisgen, E. Funke, F. C. Schaefer and R. Knorr, *Angew. Chem. Int. Ed.* 1967, **6**, 367–368; Reichardt, *Pure Appl. Chem.,* 2008, **80**, 1415–1432.

3. Catalytic experiments

In a typical catalytic procedure, phenylacetylene (88 mg, 0.86 mmol) and benzyl azide (115 mg, 0.86 mmol) were stirred with the catalyst precursor CuCl (2.6 mg, 26 μmol) and **2a** (6.5 mg, 26 μmol; 3%) for 30 min at RT without a solvent. An aliquot was dissolved in $CDCl_3$ and analysed by ^{1}H NMR spectroscopy, conversions are compiled in Table S2.

Table S2 Conversion in the cycloaddition of phenylacetylene and benzyl azide

Catalyst precursor	conversion
---	0%
CuCl	20%
2a	0%
2a + CuCl (1:1)	100%
3a	100%

4. Crystallographic details for 2a

Crystal data were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector (Mo–Kα radiation, 0.71073 Å). At least a complete dataset was collected, assuming that the Friedel pairs are equivalent. An analytical absorption correction based on the shape of the crystal was performed.[S3] The structure was solved by direct methods using the program SHELXS-97[S4] and refined by full matrix least squares on F^2 with SHELXL-97. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. Further details on data collection and refinement are summarised in Table S3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC 870677. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Table S3 Crystal data and structure refinement for **2a**

CCDC no	870677
Empirical formula	$C_{15}H_{13}N_3O$
Formula weight	251.28
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions	a = 13.9056(6) Å α = 90°
	b = 7.3192(3) Å β = 117.911(6)°
	c = 13.5734(6) Å γ = 90°
Volume	1220.77(9) Å^3
Z	4
Density (calculated)	1.367 g cm^{-3}
Absorption coefficient	0.089 mm^{-1}
F(000)	528
Crystal size	0.168 × 0.129 × 0.040 mm^3
Reflections collected	5503
Independent reflections	1933 (R_{int} = 0.0416)
Absorption correction	Analytical
Max., min. transmission	0.937, 0.807
Data, restraints, parameters	1933, 0, 173
Goodness–of–fit on F^2	1.055
Final R indices [I>2σ(I)]	R1 = 0.0404, wR2 = 0.0975
R indices (all data)	R1 = 0.0549, wR2 = 0.1055
Largest diff. peak, hole	0.172, –0.250 e Å^{-3}

Compared to **1d** (Fig. S1), the C5–N1 and the C5–C4 bonds of **2a** are longer by 0.06 Å (Table S4). The N1–N2 bond is also slightly longer. The bond lengths in the free triazolylidene **4** are between these two extremes, (0.04 Å longer than in **1d**, 0.02 Å shorter than in **2a**), which is in line with the proposed mesoionic structure. In the triazolylidene copper complex **3d**, [10a] the bonding situation is similar to that in **4**, indicating that the Cu–C bond is not a clear double bond nor a clear single bond. Obviously the electronic and steric differences between a H^+ and a [CuCl] unit will also contribute to bond length variations.

The vertex at the carbenoid carbon has been suggested as a probe for the degree of π bonding in metal NHC complexes.[S5] In **2a** with a clear C=O double bond, the C4–C5–N1 angle is slightly smaller than in **1d**, substantially larger than in the copper complex, rendering this angle a less diagnostic parameter.

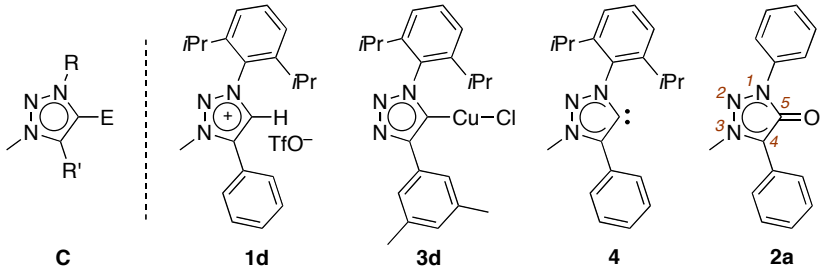

Figure S1 Generic triazolium adduct and crystallographically characterized representatives of a triazolium salt, a triazolylidene complex, and free triazolylidene (cf Table 1).

Table S4 Bond lengths (Å) and angles (°) of triazolylidenes bound to various substituents [a]

	1d [b] (E = H)	**3d** [c] (E = CuCl)	**4** [b] (E = :)	**2a** (E = O)
C5–E	0.95	1.879(5)	---	1.243(2)
C5–C4	1.3647(19)	1.404(7)	1.4053(14)	1.421(3)
C5–N1	1.3446(17)	1.382(6)	1.3662(13)	1.405(2)
N1–N2	1.3208(16)	1.326(6)	1.3439(12)	1.359(2)
N2–N3	1.3183(16)	1.336(5)	1.3216(13)	1.318(2)
N3–C4	1.3559(17)	1.370(6)	1.3682(13)	1.353(2)
C4–C5–N1	105.85(12)	101.1(4)	99.70(8)	102.33(15)

[a] atom numbering adopted to the numbering of **2a**
[b] from G. Guisado-Barrios, J. Bouffard, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.,* 2010, **49**, 4759
[c] from T. Nakamura, T. Terashima, K. Ogata and S.-I. Fukuzawa, *Org. Lett.,* 2011, **13**, 620

5. References

S1 a) D. Canseco-Gonzalez, A. Gniewek, M. Szulmanowicz, H. Müller-Bunz, A. M. Trzeciak and M. Albrecht, *Chem. Eur. J.*, 2012, DOI: 10.1002/chem.201103719. b) A. Poulain, D. Canseco-Gonzalez, R. Hynes-Roche, H. Müller-Bunz, O. Schuster, H. Stoeckli-Evans, A. Neels and M. Albrecht, *Organometallics*, 2011, **30**, 1021. c) T. Nakamura, T. Terashima, K. Ogata and S.-I. Fukuzawa, *Org. Lett.,* 2011, **13**, 620.

S2 Atomic absorption spectroscopy did not indicate any copper in the CsOH (< 1 ppm), though homeopatic doses of copper cannot be confidently excluded as actual promotor of the 'copper-free' transformation of **1** to **2**. For a relevant discussion, see: a) S. L. Buchwald and C. Bolm, *Angew. Chem. Int. Ed.,* 2009, **48**, 5586–5587; b) P.-F. Larsson, A. Correa, M. Carril, P.-O. Norrby and C. Bolm, *Angew. Chem. Int. Ed.,* 2009, **48**, 5691–5693.

S3 Program CrysalisPro Version 1.171.34.49, Agilent Technologies, 2011. Analytical numeric absorption correction using a multifaceted crystal model were based on expressions derived by Clark and Reid: R. C. Clark and J. S. Reid, *Acta Cryst.,* 1995, **A51**, 887.

S4 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

S5 X. Hu, I. Castro-Rodriguez, K. Olsen and K. Meyer, *Organometallics,* 2004, **23**, 755–764.