Electronic Supporting Information (ESI) for the manuscript

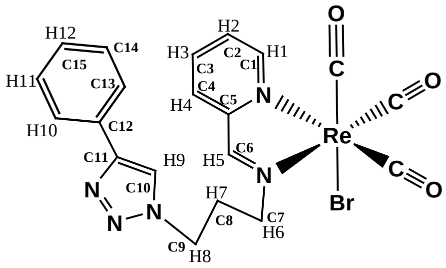
Beyond Click Chemistry: Spontaneus C-triazolyl Transfer from Copper to Rhenium and Transformation into Mesoionic C-triazolylidene Carbene

*Celedonio M. Álvarez, Luis A. García-Escudero, Raúl García-Rodríguez, Daniel Miguel**

Experimental section

General considerations. All operations were performed under an atmosphere of dry nitrogen using Schlenk and vacuum techniques. Dichloromethane and methanol were distilled from CaH_2. THF was distilled from Na/benzophenone. Hexane was distilled from Na. IR spectra in solution were recorded with a Perkin Elmer Spectrum RXI FT–IR instrument, using cells with CaF_2 windows. All NMR solvents were stored over molecular sieves and degassed prior to use. Solution NMR spectra were obtained on a Bruker AC300, Bruker AV-400, Varian MR 400 or a Varian MR 500 spectrometers. Shift values are given in ppm. ^{1}H chemical shifts are referenced to solvents. Elemental analyses were performed on a Perkin-Elmer 2400B CHN analyzer. Reagents were purchased and used without purification unless otherwise stated. 3-Azidopropan-1-amine,[1] *fac*-$[ReBr(CO)_3(pyca)]$ (**1**),[2] were prepared according to the literature procedures.

Synthesis of *fac*-$[ReBr(CO)_3\{py\text{-}2\text{-}CH{=}N\text{-}(CH_2)_3\text{-}N_3\}]$ (**2**). Compound **1** (0.200 g, 0.44 mmol) and 3-azidopropan-1-amine (0.044 g, 0.44 mmol) were refluxed in MeOH (25 ml) for 1 h. The solvent was evaporated *in vacuo*, and the resulting solid residue was dissolved in CH_2Cl_2 and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound **2** as orange microcrystals. Yield: 0.220 g, 93%. Anal. Calc. for $C_{12}H_{11}BrN_5O_3Re$: C, 26.72; H, 2.06; N, 12.98. Found: C, 27.03; H, 2.12; N, 13.22. IR (CH_2Cl_2, cm^{-1}), ν(N_3): 2105 (w); ν(CO): 2026 (vs), 1927 (s), 1903 (s). ^{1}H NMR (300 MHz, acetone-d_6, 298K): δ 9.24 (s, 1H, C*H*=N), 9.11 (d, J^3 = 5.5 Hz, 1H, py), 8.34-8.28 (m, 2H, py), 7.83 (m, 1H, py), 4.29 (t, J^3 = 6.5 Hz, 2H, CH_2), 3.58 (t, J^3 = 6.5 Hz, 2H, CH_2), 2.34 (m, 2H, $CH_2CH_2CH_2$).



Synthesis of 3. *Method A.* A mixture of **2** (0.100 g, 0.19 mmol), phenylacetylene (0.019 g, 0.19 mmol), $CuSO_4.5H_2O$ (0.005 g, 0.02 mmol) and sodium ascorbate (0.004 g, 0.02 mmol) were reacted in 4:1 THF:water (20 ml) at room temperature for 5 days. The compound was extracted with CH_2Cl_2 (3 × 15 mL), dried over magnesium sulfate, filtered and evaporated to a red precipitate. The resulting solid residue was dissolved in CH_2Cl_2 and addition of hexane and slow evaporation at reduced pressure gave compound **3** as red microcrystals. Yield: 0.095 g, 80 %. *Method B.* To a flask containing **6** (0.067 g, 0.12 mmol) in THF (15 ml) was added concentrated aqueous hydrobromic acid (0.05 ml, excess). The reaction mixture was stirred for 2 hours at reflux temperature. The solvent was evaporated *in vacuo*, and the resulting solid residue was dissolved in CH_2Cl_2. The solution was stirred with solid Na_2CO_3 (0.5 g) to neutralize the excess acid and to ensuring deprotonation of the triazole ring, dried over magnesium sulphate and filtered. Addition of hexane and slow evaporation at reduced pressure gave compound **3** as orange microcrystals. Yield: 0.072 g, 94%. Anal. Calc. for

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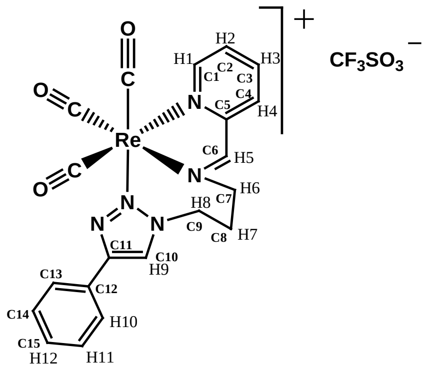
[1] V. Novakova, P. Zimcik, M. Miletin, K. Kopecky, J. Ivincova, *Tetrahedron Lett.* **2010**, *51*, 1016–1018.

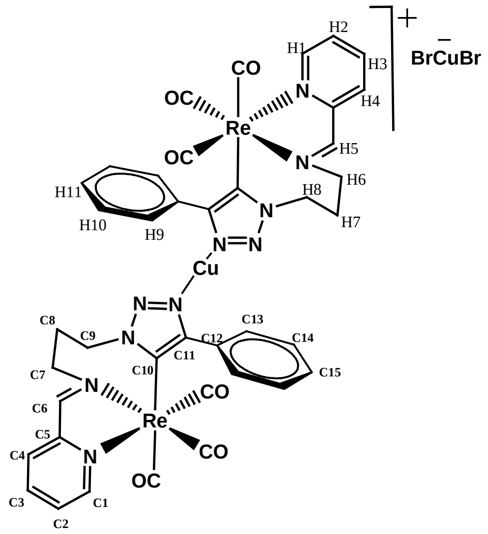
[2] C. M. Álvarez, R. García-Rodríguez, D. Miguel, *Dalton Trans.* **2007**, 3546–3554.

$C_{20}H_{17}BrN_5O_3Re$: C, 37.45; H, 2.67; N, 10.92. Found: C, 37.56; H, 2.60; N, 11.01. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2026 (vs), 1926 (s), 1904 (s). ^1H NMR (500 MHz, acetone-d_6, 298K): δ 9.22 (s, 1H, H5), 9.12 (d, J^3 = 5.0 Hz, 1H, H1), 8.45 (s, 1H, H9), 8.35-8.30 (m, 2H, H3 and H4), 7.88 (d, J^3 = 7.5 Hz, 2H, H10), 7.83 (m, 1H, H2), 7.43 (t, J^3 = 7.5 Hz, 2H, H11), 7.33 (t, J^3 = 7.5 Hz, 1H, H12), 4.76-4.61 (m, 2H, H8), 4.34-4.26 (m, 2H, H6), 2.81 (m, 1H, H7), 2.70 (m, 1H, H7). ^{13}C {^1H} NMR (125 MHz, acetone-d_6, 298 K): δ 197.2 (CO), 196.9 (CO), 186.8 (CO), 170.0 (C6), 155.2 (C5), 153.2 (C1), 147.2 (C11), 140.0 (C3 or C4), 131.3 (C12), 129.2 (C4 or C3), 128.9 (C2), 128.7 (C14), 127.7 (C15), 125.3 (C13), 120.8 (C10), 62.2 (C7), 47.1 (C9), 30.1 (C8).

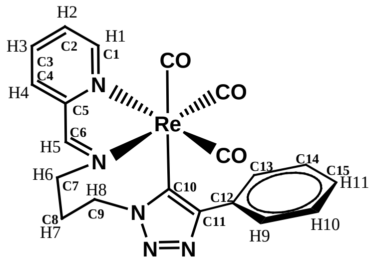


Synthesis of 4. *Method A.* To a flask containing **3** (0.070 g, 0.11 mmol) in CH_2Cl_2 (20 ml) was added AgOTf (0.028 g, 0.11 mmol). The reaction mixture was stirred for 4 hours at room temperature, and the AgBr precipitate was removed by filtration. Addition of hexane and slow evaporation at reduced pressure gave compound **4** as yellow microcrystals. Yield: 0.064 g, 83 %. *Method B.* To a flask containing **6** (0.067 g, 0.12 mmol) in THF (15 ml) was added trifluoromethanesulfonic acid (0.05 ml, excess). The reaction mixture was heated for 4 hours at reflux temperature. The solvent was evaporated *in vacuo*, and the resulting solid residue was dissolved in CH_2Cl_2. The solution was stirred with solid Na_2CO_3 (0.5 g) to neutralize the excess acid and to ensuring deprotonation of the triazole ring, dried over magnesium sulphate and filtered. Addition of hexane and slow evaporation at reduced pressure gave compound **4** as orange microcrystals. Yield: 0.077 g, 90%. Anal. Calc. for $C_{21}H_{17}N_5O_6F_3SRe$: C, 35.49; H, 2.41; N, 9.85. Found: C, 35.49; H, 2.50; N, 9.77. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2038 (vs), 1936 (s), 1922 (s). ^1H NMR (500 MHz, acetone-d_6, 298K): δ 9.47 (d, J^3 = 5.5 Hz, 1H, H1), 9.35 (s, 1H, H5), 8.83 (s, 1H, H9), 8.40-8.36 (m, 1H, H3), 8.21 (d, J^3 = 5.5 Hz, H4), 8.07-8.03 (m, 1H, H2), 7.69-7.65 (m, 2H, H10), 7.43-7.34 (m, 3H, H11 and H12), 5.30-5.16 (m, 2H, H8), 4.93-4.86 (m, 1H, H6), 4.83-4.75 (m, 1H, H6), 2.89-2.81 (m, 1H, H7), 2.48-2.36 (m, 1H, H7). ^{13}C {^1H} NMR (125 MHz, acetone-d_6, 298 K): δ 195.7 (CO), 194.5 (CO), 190.0 (CO), 174.3 (C6), 155.3 (C5), 154.3 (C1), 148.3 (C11), 141.4 (C3), 130.3 (C2), 129.2 (C4), 129.1 (C15), 129.0 (C14), 128.6 (C12), 127.3 (C10), 125.4 (C13), 64.1 (C9), 51.7 (C7), 32.6 (C8).

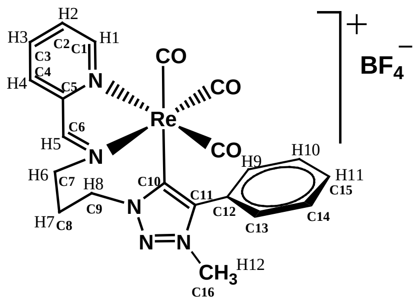
The triazole ring in compound **4** is depicted tentatively as coordinated through the central N2 atom, whereas in compound **5** it is found to be coordinated through N3. An inspection with molecular models showed that coordination through N3 in **4** would lead to a highly tensioned arrangement. On the other hand, coordination through the central N2 have been found in related complexes with triazole tethered through N1 (see compounds in ref 5) while coordination through N3 is usually found in triazole tethered through one of the carbon atoms. Unfortunately, despite many attempts, it has not been possible to grow a crystal of **4** suitable for X-ray crystallography.



Synthesis of 5. *Method A.* A mixture of **2** (0.100 g, 0.18 mmol), phenylacetylene (0.023 g, 0.22 mmol), $CuSO_4.5H_2O$ (0.055 g, 0.22 mmol) and sodium ascorbate (0.043 g, 0.22 mmol) were reacted in 4:1 THF:water (25 ml) at reflux temperature for 1 hour. The compound was extracted with CH_2Cl_2 (3 × 25 ml), dried over magnesium sulphate, filtered and evaporated to an orange precipitate. The resulting solid residue was dissolved in CH_2Cl_2 and addition of hexane and slow diffusion gave compound **5** as yellow-orange microcrystals. Yield: 0.089 g, 79%. *Method B.* A mixture of **1** (0.050 g, 0.11 mmol), and 3-azidopropan-1-amine (0.011 g, 0.11 mmol), was refluxed in THF (20 ml). IR monitoring showed the formation of **2** after 2h. To the solution were then added phenylacetylene (0.014 g, 0.13 mmol), $CuSO_4.5H_2O$ (0.032 g, 0.13 mmol), sodium ascorbate (0.026 g, 0.13 mmol) and water (5 ml) and the mixture was heated at reflux temperature for 1 hour and then evaporated under vacuum. The orange residue was extracted with CH_2Cl_2 (3 × 15 ml) and dried over magnesium sulphate. Addition of hexane and slow evaporation gave compound **5** as yellow-orange microcrystals. Yield: 0.050 g, 72%. Anal. Calc. for $C_{28}H_{22}Cu_2Br_2N_{10}O_6Re_2$: C, 26.82; H, 1.77; N, 11.17. Found: C, 26.96; H, 1.83; N, 11.27. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2017 (vs), 1921 (s), 1904 (s). ^1H NMR (300 MHz, acetone-d_6, 298K): δ 9.00 (s, 1H, H5), 8.06-7.99 (m, 2H, H3 and H4), 7.97 (d, J^3 = 5,5 Hz, 1H, H1), 7.40 (t, J^3 = 7.0 Hz, 1H, H11), 7.28 (t, J^3 = 7.0 Hz, 2H, H10), 7.12 (d, J^3 = 7.0 Hz, 2H, H9),7.09-7.05 (m, 1H, H2), 5.15-4.98 (m, 2H, H8), 4.75-4.58 (m, 2H, H6), 2.74-2.55 (m, 1H, H7) 2.05-1.96 (m, 1H, H7). ^{13}C {^1H} NMR (125 MHz, acetone-d_6, 298 K): δ 200.4 (CO), 198.6 (CO), 191.6 (CO), 170.2 (C6), 155.5 (C12), 155.4 (C5), 153.9 (C1), 153.8 (C10), 139.7 (C3 or C4), 135.8 (C11), 130.7 (C13), 129.5 (C4 or C3), 129.1 (C14), 128.7 (C2), 128.5 (C15), 65.5 (C7), 52.0 (C9), 35.2 (C8).



Synthesis of 6. To a flask containing **5** (0.100 g, 0.18 mmol) in CH_2Cl_2 (15 mL) was added concentrated ammonia solution (10 ml). The reaction mixture was stirred for 3 hours at room temperature. The compound was extracted with CH_2Cl_2 (3 × 10 ml), the organic layers were combined, dried over magnesium sulphate and filtered. Addition of hexane and slow evaporation at reduced pressure gave compound **6** as orange microcrystals. Yield: 0.084 g, 94%. Anal. Calc. for $C_{20}H_{16}N_5O_3Re$: C, 42.85; H, 2.88; N, 12.49. Found: C, 43.00; H, 2.80; N, 12.54. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2012 (vs), 1912 (s), 1899 (s). ^1H NMR (500 MHz, acetone-d_6, 298K): δ 8.91 (s, 1H, H5), 8.00 (d, J^3 = 5.5 Hz, 1H, H1), 7.98-7.91 (m, 2H, H3 and H4), 7.29-7.24 (m, 1H, H11), 7.22-7.17 (m, 2H, H10), 7.15-7.11 (m, 2H, H9), 7.00-6.95 (m, 1H, H2), 5.00-4.90 (m, 2H, H8), 4.67-4.55 (m, 2H, H6), 2.63-2.55 (m, 1H, H7), 2.01-1.91 (m, 1H, H7). ^{13}C {^1H} NMR (125 MHz, acetone-d_6, 298 K): δ 201.2 (CO), 199.3 (CO), 191.8 (CO), 169.5 (C6), 156.2 (C12), 155.4 (C5), 153.8 (C1), 153.5 (C10), 139.4 (C3 or C4), 138.6 (C11), 130.3 (C13), 129.1 (C4 or C3), 128.5 (C14), 127.9 (C2), 127.1 (C15), 65.5 (C7), 50.7 (C9), 35.7 (C8).



Synthesis of 7. To a flask containing **6** (0.067 g, 0.12 mmol) in CH_2Cl_2 (15 ml) was added trimethyloxonium tetrafluoroborate. (0.018 g, 0.12 mmol). The reaction mixture was stirred for 15 minutes at room temperature. Addition of hexane and slow evaporation at reduced pressure gave compound **7** as orange microcrystals. Yield: 0.070 g, 89%. Anal. Calc. for $C_{21}H_{19}BF_4N_5O_3Re$: C, 38.08; H, 2.89; N, 10.57. Found: C, 38.12; H, 2.83; N, 10.67. IR (CH_2Cl_2, cm^{-1}), ν(CO): 2023 (vs), 1923 (s), 1905 (s). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ 8.84 (s, 1H, H5), 8.01 (d, J^3 = 7.5 Hz, 1H, H4), 7.89 (td, J^3 = 7.5 Hz and J^4 = 1.5 Hz, 1H, H3), 7.67 (d, J^3 = 5.5 Hz, 1H, H1), 7.54 (t, J^3 = 7.5 Hz, 1H, H11), 7.51-7.23 (s, br, 4H, H9 and H10), 6.92-6.87 (m, 1H, H2), 5.21-5.13 (m, 1H, H8), 5.03-4.95 (m, 1H, H8), 4.63-4.47 (m, 1H, H6), 3.71 (s, 3H, H12) 2.61-2.32 (m, 2H, H7). ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2, 298 K): δ 198.3 (CO), 196.9 (CO), 190.1 (CO), 171.2 (C6), 162.1 (C10), 155.2 (C5), 152.5 (C1), 148.9 (C11), 138.9 (C3), 130.6 (C15), 130.0 (C4), 129.43 (C13 and C14), 128.0 (C2), 127.2 (C12), 64.7 (C7), 53.9 (C9), 36.8 (C16), 32.8 (C8).

Crystallographic data of compounds 2, 5, 6, and 7.

Intensities measurements for **2**, **6**, and **7** were made with a Oxford Diffraction Super Nova diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. Compound Data collection and integration, and phase indexing absorption corection were done with the program CrysAlisPro.[3] The crystal of **5** was measured with a Bruker AXS SMART 1000 diffractometer with graphite monochromatized Mo Kα X-radiation and a CCD area detector. Raw frame data were integrated with the SAINT program.[4] A semi-empirical absorption correction was applied with the program SADABS.[5]

The structures were solved by direct methods with SIR2002,[6] under WINGX,[7] and refined against F^2 with SHELXTL.[8] All non-hydrogen atoms were refined anisotropically unless otherwise stated. Calculations were made with SHELXTL and PARST,[9] and graphics were made with SHELXTL and MERCURY.[10]

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[3] CrysAlisPro-Data collection and integration software. Oxford Diffraction Ltd. **2009**.

[4] SAINT+. SAX area detector integration program. Version 6.02. Bruker AXS, Inc. Madison, WI, 1999.

[5] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 1997.

[6] Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidory, G.; Spagna, R. *SIR2002, A program for automatic solution and refinement of crystal structures. J. Appl. Cryst.* **2003**, *36*, 1103.

[7] Farrugia, L.J. *J. Appl. Cryst.*, **1999**, *32*, 837-838.

[8] Sheldrick G. M *Acta Cryst.* **2008**, *A64*, 112-122. Sheldrick, G. M. SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1. Bruker AXS, Inc. Madison, WI, **1998**.

[9] *(a)* Nardelli, M. *Comput. Chem.*, 1983, **7**, 95-97. *(b)* Nardelli, M. *J. Appl. Crystallogr.*, **1995**, *28*, 659.

[10] MERCURY: a) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M. K.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr.*, 2002, **B58**, 389-397. b) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.*, **2006**, *39*, 453-457.

Table S1. Crystallographic data for compounds 2, 5, 6 and 7.

Compound reference	Compound 2	Compound 5	Compound 6	Compound 7
Chemical formula	$C_{12}H_{11}BrN_5O_3Re$	$C_{20}H_{16}BrCuN_5O_3Re$	$C_{20}H_{16}N_5O_3Re$	$C_{22}H_{21}BCl_2F_4N_5O_3Re$
Formula Mass	539.37	704.03	560.58	747.35
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
a/Å	13.9080(11)	8.833(4)	7.2895(5)	33.0420(7)
b/Å	9.1333(5)	9.312(4)	9.7173(7)	13.0010(2)
c/Å	13.1805(7)	14.440(7)	15.3974(10)	27.7310(7)
α/°	90.00	71.824(9)	73.505(6)	90.00
β/°	101.093(6)	77.963(9)	86.389(5)	113.570(3)
γ/°	90.00	78.790(10)	70.454(6)	90.00
Unit cell volume/Å^3	1642.99(18)	1092.9(9)	984.90(11)	10918.8(4)
Temperature/K	293(2)	298(2)	293(2)	293(2)
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
No. of formula units per unit cell, Z	4	2	2	16
No. of reflections measured	8215	5006	6327	21036
No. of independent reflections	3863	3106	3906	10871
R_{int}	0.0459	0.0697	0.0422	0.0328
Final R_1 values ($I > 2\sigma(I)$)	0.0455	0.0734	0.0393	0.0456
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0917	0.1618	0.0931	0.1157
Final R_1 values (all data)	0.0650	0.1302	0.0439	0.0670
Final $wR(F^2)$ values (all data)	0.1061	0.1890	0.0984	0.1310
Goodness of fit on F^2	1.040	0.981	1.083	1.046
CCDC number	867717	867718	867719	867720

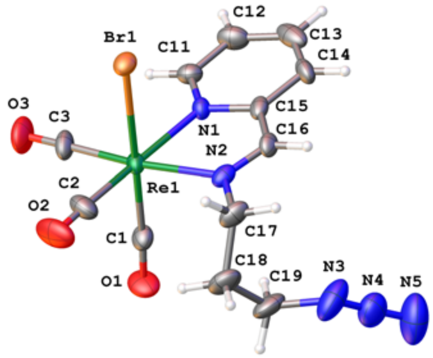

Figure S1. Perspective view of **2**, showing the atom numbering.