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COMMUNICATION

Sterically driven synthesis of ruthenium and ruthenium-silver *N*-heterocyclic carbene complexes

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A straightforward and efficient synthetic route to novel Ru *N*-heterocyclic carbenes (NHC) complexes by transmetalation of non-bulky silver NHC to ruthenium dicarbonyl tetraarylcyclopentadienone is described. The same procedure with sterically demanding NHC leads to unprecedented heterobimetallic Ru-Ag(NHC) complexes.

Ruthenium based *N*-heterocyclic carbene complexes are among the most versatile homogeneous catalysts. In addition to the well-known second generation Grubb's metathesis catalysts,¹ Ru(NHC) catalysts have found application in a broad variety of reactions,² including: transfer hydrogenation,³ hydrogenation of olefins⁴ and esters,⁵ asymmetric hydrogenation,⁶ amide synthesis from alcohols and nitriles,⁷ dehydrogenation of esters and imines from alcohols,⁸ racemization of chiral alcohols,⁹ alcohol¹⁰ and water oxidation.¹¹ Moreover, Ru(NHC) are also employed in medical and material science as potential antitumoral drugs,¹² and in the development of sensitizers.¹³ From a more general perspective *N*-heterocyclic carbenes (NHCs) are widely documented as ubiquitous ancillary ligands due to their strong coordination ability and the tuneable character of their steric and electronic properties.¹⁴

Another class of versatile ligands is represented by tetraarylcyclopentadienones, which behave as non-innocent ligands in reactions promoted by the well-known ruthenium based Shvo catalyst.¹⁵

Since our research interests recently focused on both *N*-heterocyclic carbenes¹⁶ and cyclopentadienone ligands,¹⁷ we wondered about the possibility to exploit both ligands in the preparation of novel Ru(0) complexes. Indeed, most of the literature on Ru(NHC) complexes, is based on Ru(II), whereas the chemistry of Ru(0)(NHC) is essentially limited to the combination of NHCs (or their precursors) with Ru₃(CO)₁₂ and Ru(CO)₂(PPh₃)₃.¹⁸

We herein report the sterically driven synthesis of ruthenium(0) and ruthenium-silver dicarbonyl tetraarylcyclopentadienone *N*-heterocyclic carbene complexes.

As a first step, we prepared a small library of variously encumbered imidazolium salts, by following procedures reported in the literature (Chart 1, ESI)

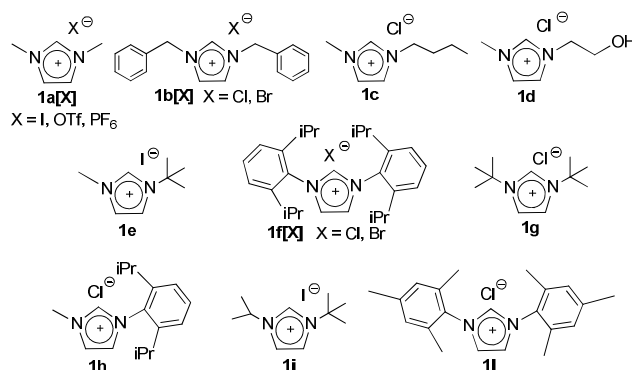
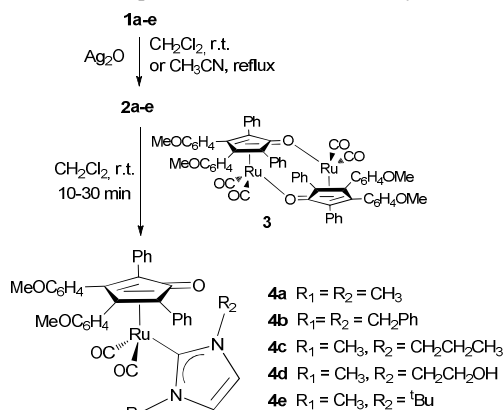


Chart 1 Imidazolium salts precursors of NHC ligands.

At a later stage, imidazolium salts **1a-e** have been reacted with Ag₂O and the corresponding silver complexes (**2**, ESI) directly treated *in situ* with the dimeric precursor dicarbonyl(η⁴-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) (**3**). A quantitative and instant transmetalation reaction leads to the formation of the neutral Ru(0) complexes **4a-e** (Scheme 1). The reaction is general with non-bulky *N*-heterocyclic carbenes and tolerant to functional groups, in fact it occurs in the presence of a primary alcohol in the lateral chain (**1d** to **4d**) without the need of protection. The synthesis of **4a-e** has been followed by IR spectroscopy observing in all the cases a lowering in the CO stretching frequencies (e.g. **4a**: ν(CO) = 2004, 1945 cm⁻¹ vs. **3**: 2018, 1967 cm⁻¹) due to the strong σ donor properties of *N*-heterocyclic carbenes. IR spectra are very similar for complexes **4a-c**, whereas, in the case of the hydroxyl-functionalized complex **4d**, increased frequency for terminal CO and lowering of cyclopentadienone ν C=O are observed [ν(CO) = 2011, 1952 cm⁻¹; ν(C=O) = 1558 cm⁻¹ vs. 1586 cm⁻¹ for **4a**] which is ascribable to the formation of hydrogen bond between -OH and the carbonyl group, as

demonstrated by X-Ray diffraction. ^{13}C -NMRs show a diagnostic signal for the $\text{Ru}-\text{C}_{\text{carbene}}$ within the range 172–173 ppm and molecular ions of complexes **4a–e** are detectable by ESI-MS (ESI).



Scheme 1 Synthesis of dicarbonyl-cyclopentadienone-*N*-heterocyclic carbene ruthenium complexes (**4a–e**).

Complexes **4a**, **4b** and **4d** have been also characterized by X-Ray diffraction studies. The molecular structure of **4a** is reported in Fig. 1, whereas those of **4b** and **4d** as well a list of their main bonding parameters are given as Supporting Information (Figs. S1 and S2, Table S1). The three complexes display almost identical structures, apart from the different substituents on the *N*-heterocyclic carbene ligand. The $\text{Ru}(1)-\text{C}(3)$ distance [2.471(3) Å in **4a**] is significantly longer than $\text{Ru}(1)-\text{C}(4-7)$ [2.206(3)–2.274(3) Å, average 2.238(7) Å in **4a**] and $\text{C}(3)-\text{O}(3)$ [1.247(4) Å] is essentially a double bond.¹⁹ The $\text{Ru}(1)-\text{C}(34)$ contact [2.118(4) Å] is in the typical range for the interaction between $\text{Ru}(0)$ and a *N*-heterocyclic carbene.^{18a}

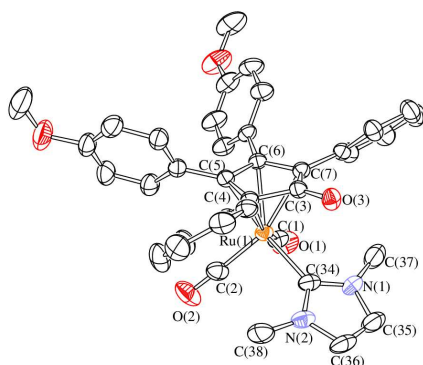
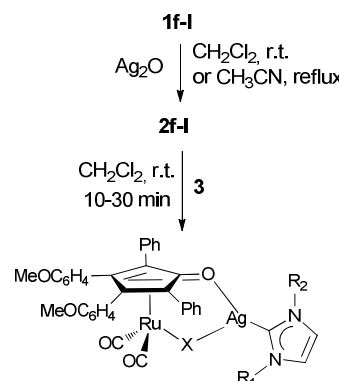


Fig. 1 ORTEP drawing of **4a**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): $\text{Ru}(1)-\text{C}(1)$ 1.892(5), $\text{Ru}(1)-\text{C}(2)$ 1.881(5), $\text{Ru}(1)-\text{C}(3)$ 2.471(3), $\text{Ru}(1)-\text{C}(4)$ 2.263(3), $\text{Ru}(1)-\text{C}(5)$ 2.206(3), $\text{Ru}(1)-\text{C}(6)$ 2.211(3), $\text{Ru}(1)-\text{C}(7)$ 2.274(3), $\text{Ru}(1)-\text{C}(34)$ 2.118(4), $\text{C}(3)-\text{O}(3)$ 1.247(4).

The use of the more sterically hindered imidazolium salts **1f–i** led to the unexpected hitherto unreported heterodimetallic ruthenium-silver complexes of type **5** (Scheme 2). As reviewed by Kuhl,²⁰ implications of the wingtip groups in *N*-heterocyclic carbene complexes are normally ascribable to steric factors, and this is also our case, in that encumbrance arise by both the tetraarylcyclopentadienone and the *N*-heterocyclic carbene moiety. On the other hand, a possible role of the donor properties of NHCs, in addition to their steric effects should not be excluded. Indeed, NHCs with bulky substituents generally display better donor properties, as evaluated by TEP values (Tolman Electronic Parameters).²¹ For example, **1g** containing *t*-butyl groups is a better

donor compared to **1a**, containing methyls.^{21a} A combination of these steric and electronic effects might increase both stability and inertness of the silver complexes intermediates (in case of **2f–i**) and consequently disfavor carbene transmetalation compared with halide coordination. If this hypothesis is realistic the observed formation of bimetallic products, in the case of bulky NHCs, should be the consequence of both steric congestion at the ruthenium products and lower tendency to transmetalation of the silver intermediates.

This remarkable reactivity is likely to be favored by the formation of a $\text{Ru}-\text{Cl}-\text{Ag}$ bridge and by the concomitant interaction between the silver metal and the carbonyl of the cyclopentadienone.



5f[Cl] $\text{X} = \text{Cl}$, $\text{R}_1 = \text{R}_2 = 2,6(\text{iPr})_2\text{Ph}$; **5f[Br]** $\text{X} = \text{Br}$, $\text{R}_1 = \text{R}_2 = 2,6(\text{iPr})_2\text{Ph}$
5g $\text{X} = \text{Cl}$, $\text{R}_1 = \text{R}_2 = \text{tBu}$; **5h** $\text{X} = \text{I}$, $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = 2,6(\text{iPr})_2\text{Ph}$;
5i $\text{X} = \text{I}$, $\text{R}_1 = \text{iPr}$, $\text{R}_2 = \text{tBu}$; **5l** $\text{X} = \text{I}$, $\text{R}_1 = \text{Mes}$, $\text{R}_2 = \text{Mes}$

Scheme 2 Synthesis of heterodimetallic Ru-Ag complexes (**5f–i**).

The dinuclear complexes **5f–i** have been characterized by IR, ^1H and ^{13}C -NMR and ESI-MS (ESI). Suitable crystals for X-Ray diffraction have been obtained for **5f[Cl]**. FT-IR CO stretching frequencies are in the range 2013–2014 and 1953–1955 cm^{-1} , while at the ^{13}C -NMR spectra the $\text{Ag}-\text{C}_{\text{carbene}}$ resonates as a doublet of doublet (e.g. **5f[Cl]**: 188.6 ppm; dd, $J(^{109}\text{Ag}-^{13}\text{C}) = 271 \text{ Hz}$; $J(^{108}\text{Ag}-^{13}\text{C}) = 235 \text{ Hz}$). The structure of **5f[Cl]** has been crystallographically determined (Fig. 2 and Table S2). This is composed by a $\text{RuCl}(\text{CO})_2$ (tetraarylcyclopentadienone) moiety chelating on the $\text{Ag}(\text{N-heterocyclic carbene})$ via $\text{O}(3)$ and $\text{Cl}(1)$. The $\text{C}(3)-\text{O}(3)$ distance [1.248(7) Å] is almost identical to the one found in **4a** [1.245(4) Å] retaining its double bond character and suggesting a dative bond between $\text{O}(3)$ and $\text{Ag}(1)$.

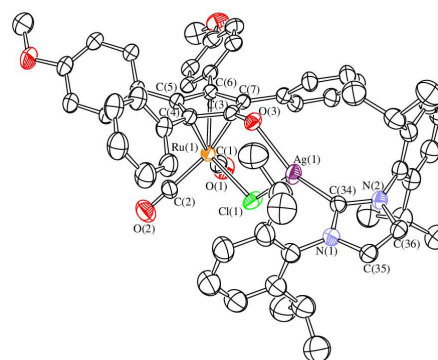
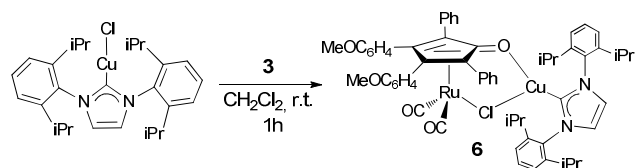


Fig. 2 ORTEP drawing of **5f[Cl]**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): $\text{Ru}(1)-\text{C}(1)$ 1.877(8), $\text{Ru}(1)-\text{C}(2)$ 1.864(8), $\text{Ru}(1)-\text{C}(3)$ 2.425(6), $\text{Ru}(1)-\text{C}(4)$ 2.251(6), $\text{Ru}(1)-\text{C}(5)$ 2.199(6), $\text{Ru}(1)-\text{C}(6)$ 2.193(6), $\text{Ru}(1)-\text{C}(7)$ 2.243(6), $\text{Ru}(1)-\text{Cl}(1)$ 2.4379(17), $\text{C}(3)-\text{O}(3)$ 1.248(7), $\text{Ag}(1)-\text{O}(3)$ 2.222(4), $\text{Ag}(1)-\text{Cl}(1)$ 2.6277(18), $\text{Ag}(1)-\text{C}(34)$ 2.090(6).

Once investigated the substrate scope, we have extended our studies to copper. The reaction between 1,3-di-(2,6-diisopropylphenyl)imidazole-2-ylidene copper chloride and **3** confirmed the same reactivity as demonstrated by X-Ray crystal structure of the Ru-Cl-Cu-O complex **6** (Figure S3 and Table S2).



Scheme 3 Synthesis of heterodimetallic Ru-Cu complex (**6**).

The heterodimetallic complexes **5** and **6** are stable in the solid state, while in solution they decompose in more than 24h.

In summary, a very efficient and rapid synthetic route for obtaining novel Ru(0) complexes, which combine *N*-heterocyclic carbenes and tetraarylcyclopentadienone ligands, has been found. The reaction scope is general and transmetalation proved to be tolerant to primary alcohol. A role of the steric hindrance of the ligands has been observed leading to the remarkable formation of heterobimetallic complexes containing both Ru and Ag or Cu. The novel synthetic methods for the preparation of complexes of type **4**, **5** and **6** pave the way for future developments in both homogeneous catalysis and medical applications.

Notes and references

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Electronic Supplementary Information (ESI) available: experimental details for complexes **2**, **3**, **4a-e**, **5f-i** and **6** (¹H-NMR, ¹³C-NMR, IR, ESI-MS, elemental analyses, X-Ray diffraction). See DOI: 10.1039/c000000x/ The authors wish to thank the Ministero dell'Università e della Ricerca (MIUR) ("Designing metal containing molecular fragments for advanced chemical applications") and the University of Bologna for financial support.

- (a) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.*, 2010, **110**, 1746; A. H. Hoveyda, S. J. Malcolmson, S. J. Meek and A. R. Zhugralin, *Angew. Chem. Int. Ed.*, 2010, **49**, 34; (b) S. P. Nolan and H. Clavier, *Chem. Soc. Rev.*, 2010, **39**, 3305.
- (a) S. Diez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612; (b) H. D. Velazquez and F. Verpoort, *Chem. Soc. Rev.*, 2012, **41**, 7032.
- (a) J. Witt, A. Pothig, F. E. Kuhn, W. Baratta, *Organometallics*, 2013, **32**, 4042; (b) N. Gurbuz, E. O. Ozcan, I. Ozdemir, B. Cetinkaya, O. Sahin and O. Buyukgungor, *Dalton Trans.*, 2012, **41**, 2330; (c) S. Horn, C. Gandolfi and M. Albrecht, *Eur. J. Inorg. Chem.*, 2011, 2863; (d) S. Kuwata and T. Ikariya, *Chem. Eur. J.*, 2011, **17**, 3542; (e) H. Ohara, W. W. N. O, A. J. Lough and R. H. Morris, *Dalton Trans.*, 2012, **41**, 8797; (f) W. W. N. O, A. J. Lough and R. H. Morris, *Organometallics*, 2012, **31**, 2137.
- T. Wang, C. Pranckevicius, C. L. Lund, M. J. Sgro and D. W. Stephan, *Organometallics*, 2013, **32**, 2168 and references cited therein.
- E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon and D. Milstein, *Organometallics*, 2011, **30**, 3826.
- (a) S. Urban, B. Beiring, N. Ortega, D. Paul and F. Glorius, *J. Am. Chem. Soc.*, 2012, **134**, 1541; (b) J. Wysocki, N. Ortega and F. Glorius, *Angew. Chem. Int. Ed.*, 2014, **53**, 8751.
- B. Kang, Z. Fu and S. H. Hong, *J. Am. Chem. Soc.*, 2013, **135**, 11704.
- I. S. Makarov and R. Madsen, *J. Org. Chem.*, 2013, **78**, 6593 and references cited therein.
- J. Balogh, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2012, **31**, 3259.
- (a) A. Prades, E. Peris and M. Albrecht, *Organometallics*, 2011, **30**, 1162; (b) D. Canseco-Gonzalez and M. Albrecht, *Dalton Trans.*, 2013, **42**, 7424.
- L. Bernet, R. Larlempuia, W. Ghattas, H. Mueller-Bunz, L. Vigara, A. Llobet and M. Albrecht, *Chem. Commun.*, 2011, **47**, 8058.
- (a) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, **109**, 2009, 3445; (b) K. M. Hindi, M. J. Panzer, C. A. Tessier, C. L. Cannon, W. J. Youngs, *Chem. Rev.*, 2009, **109**, 3859; (c) A. Monney, M. Albrecht, *Coord. Chem. Rev.*, 2013, **257**, 2420; (d) W. Liu, R. Gust, *Chem. Soc. Rev.*, 2013, **42**, 755.
- (a) V. Leigh, W. Ghattas, R. Larlempuia, H. Muller-Bunz, M. T. Pryce and M. Albrecht, *Inorg. Chem.*, 2013, **52**, 5395; (b) S. Sinn, B. Schultze, C. Friebe, D. G. Brown, M. Jager, E. Altuntas, J. Kubel, O. Gunter, C. P. Berlinguette, B. Dietzek and U. S. Schubert, *Inorg. Chem.*, 2014, **53**, 2083; (c) W.-C. Chang, H.-S. Chen, T.-Y. Li, N.-M. Hsu, Y. S. Tingare, C.-Y. Li, Y.-C. Liu, C. Su and W.-R. Li, *Angew. Chem., Int. Ed.*, 2010, **49**, 8161.
- Selected reviews on *N*-heterocyclic carbenes: (a) L. A. Schaper, S. J. Hock, W. A. Herrmann and F. E. Kuhn, *Angew. Chem., Int. Ed.*, 2013, **52**, 270; (b) K. F. Donnelly, A. Petronilho and M. Albrecht, *Chem. Commun.*, 2013, **49**, 1145; (c) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Lapontaz and V. Césari, *Chem. Rev.*, 2011, **111**, 2705; (d) L. Merce and M. Albrecht, *Chem. Soc. Rev.*, 2010, **39**, 1903; (e) H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687; (f) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247; (g) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (h) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.
- (a) M. C. Warner, C. P. Casey and J.-E. Backvall, *Top. Organomet. Chem.*, 2011, **37**, 85; (b) B. L. Conley, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294; (c) T. Pasini, G. Solinas, V. Zanotti, S. Albonetti, F. Cavani, A. Vaccari, A. Mazzanti, S. Ranieri and R. Mazzoni, *Dalton Trans.*, 2014, **43**, 10224.
- (a) L. Busetto, M. C. Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni and G. Solinas, *Organometallics*, 2011, **30**, 5258; (b) M. C. Cassani, M. A. Brucka, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni and G. Solinas, *New J. Chem.*, 2014, **38**, 1768.
- (a) C. Cesari, L. Sambri, S. Zacchini, V. Zanotti and R. Mazzoni, *Organometallics*, 2014, **33**, 2814; (b) M. Boiani, A. Baschieri, C. Cesari, R. Mazzoni, S. Stagni, S. Zacchini and L. Sambri, *New J. Chem.*, 2012, **36**, 1469.
- See for examples: (a) J. A. Cabeza and P. Garcia-Alvarez, *Chem. Soc. Rev.*, 2011, **40**, 5389; (b) J. A. Cabeza, M. Damonte and E. Perez-Carreno, *Organometallics*, 2012, **31**, 8355; (c) J. A. Cabeza, M. Damonte, P. Garcia-Alvarez and E. Perez-Carreno, *Chem. Commun.*,

- 2013, **49**, 2813; (d) C. E. Ellul, M. F. Mahon, O. Saker and M. K. Whittlesey, *Angew. Chem. Int. Ed.*, 2007, **46**, 6343; (e) L. Benhamou, J. Wolf, V. Cesar, A. Labande, R. Poli, N. Lugan and G. Lavigne, *Organometallics*, 2009, **28**, 6981.
- 19 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans.*, 1987, **2**, S1-S19.
- 20 O. Kuhl, *Coord. Chem. Rev.*, 2009, **253**, 2481.
- 21 (a) D. G. Gusev, *Organometallics*, 2009, **28**, 6458; (b) R. Tonner and G. Frenking, *Organometallics*, 2009, **28**, 3901; (c) A. Furstner, M. Alcarazo, H. Krause and C. W. Lehmann, *J. Am. Chem. Soc.*, 2007, **129**, 12676.

Entry for the Table of Contents

A sterically driven synthetic route from non-bulky silver NHC to novel Ru(NHC) complexes and from bulky Ag(NHC) to unprecedented heterobimetallic Ru-Ag(NHC) complexes is presented.

