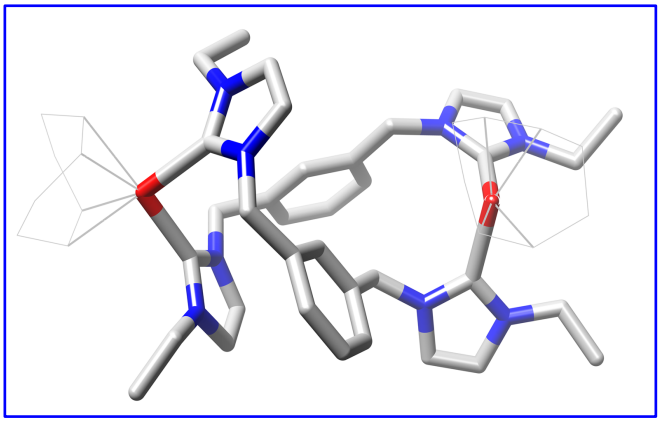
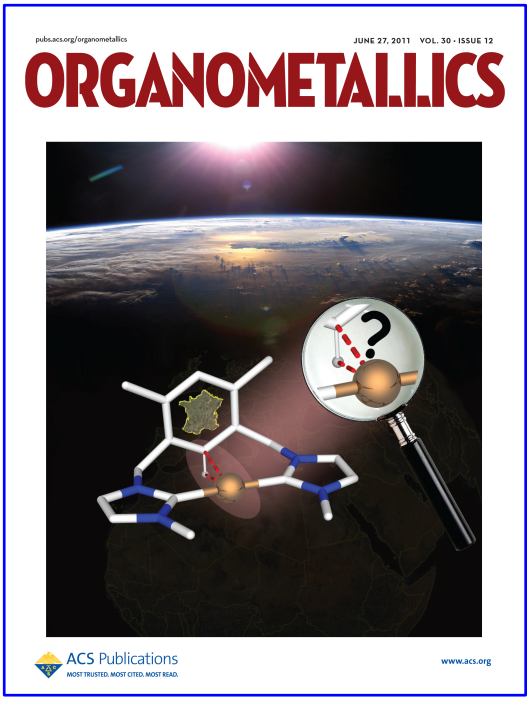
3) *N-Heterocyclic Carbene Chemistry*

N-heterocyclic carbenes have become ubiquitous ligands in organometallic and coordination chemistry and in homogeneous catalysis.

To discover new catalysts for the C-H activation of alkanes, we initiated a programme in 2008 aimed at developing synthetic methodologies toward dinuclear Ir complexes containing bis-NHC ligands. He characterised a range of mono- and dinuclear iridium-bis(N-heterocyclic carbene), including unprecedented, figure-of-eight, dinuclear iridium(I) dicarbene and iridium(III) « pincer » complexes (*Chem. Commun.*, 2008, 3983).



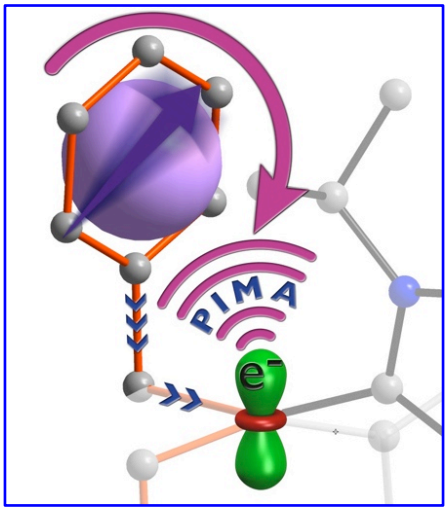
The isolation of numerous reaction intermediates represents an important contribution to a better understanding of the elementary steps involved in the formation of chelating or pincer-type ligands as a function of the spacer between the NHC donors. We reported unusual bonding features where metal-ligand proximity does not necessarily imply bonding interactions and found that Cu NHC complexes can be used for transmetallation in place of the common Ag NHC reagents.



X. Liu, R. Pattacini, P. Deglmann, P. Braunstein
Do short C-H-M (M = Cu(I), Ag(I)) distances represent agostic interactions in pincer-type complexes? Unusual NHC transmetalation from Cu(I) to Ag(I).
Organometallics, **2011**, *30*, 3302-3310

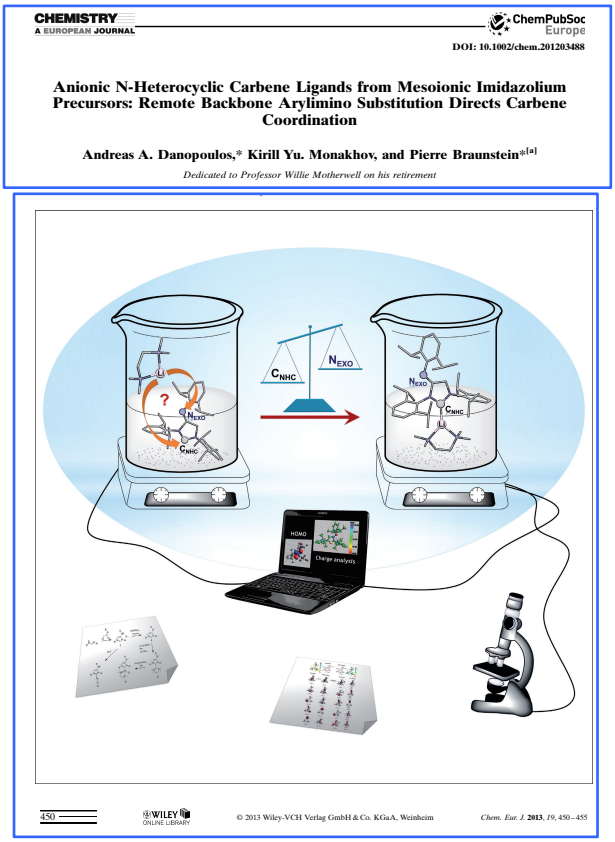
(*Comments from the Editor:* ***The first cover of this journal to originate from France*** *features a molecule that was synthesized in Strasbourg by an international team of chemists from China, Germany, Italy, and France under the leadership of P. Braunstein. Their work analyses the bonding in novel bis(NHC) Cu(I) and Ag(I) complexes in which the aryl spacer between the NHC ligands is in close proximity to the metal. However, proximity does not always imply bonding!*)

An important combined experimental/theoretical study dealt with the remarkable bending of benzyl ligands in unprecedented open-shell organometallic Cr^{II} complexes. It was found that this bending is controlled by a type of intramolecular, non-covalent interaction, coined *Polarisation-Induced Metal-Arene* (PIMA) interaction, that is expected to have chemical implications in reactivity and catalysis.



A. A. Danopoulos, K. Yu. Monakhov, V. Robert, P. Braunstein, R. Pattacini, S. Conde-Guadaño, M. Hanton, R. P. Tooze. Angular Distortions at Benzylic Carbons due to Intra-molecular Polarization-Induced Metal–Arene Interactions: a Case Study with Open-Shell Cr(II) NHC Complexes *Organometallics*, **2013**, *32*, 1842-1850.

We obtained novel anionic NHC ligands from mesoionic imidazolium precursors and found that the remote backbone arylimino substitution directs carbene coordination. This opens the way to a range of mono- or dinuclear metal complexes with electronically and sterically tunable ligands.


CHEMISTRY
A EUROPEAN JOURNAL
ChemPubSoc Europe
DOI: 10.1002/chem.201203488

Anionic N-Heterocyclic Carbene Ligands from Mesoionic Imidazolium Precursors: Remote Backbone Arylimino Substitution Directs Carbene Coordination

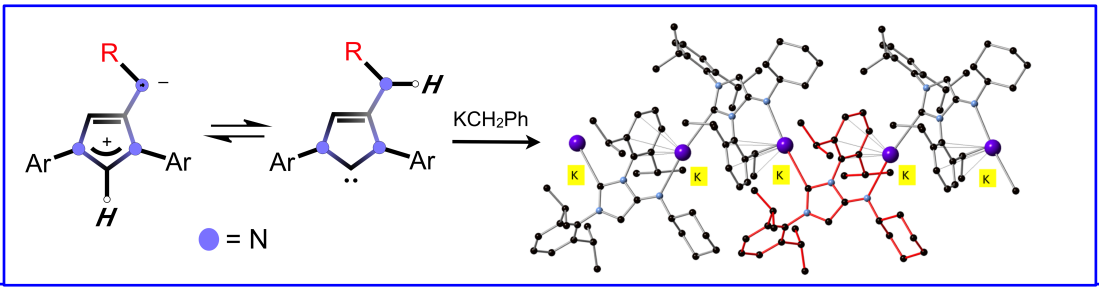
Andreas A. Danopoulos,* Kirill Yu. Monakhov, and Pierre Braunstein*[a]

Dedicated to Professor Willie Motherwell on his retirement

A. A. Danopoulos,* K. Yu. Monakhov, P. Braunstein* Anionic NHC Ligands from Mesoionic Imidazolium Precursors: Remote Backbone Arylimino Substitution Directs Carbene Coordination
Chem. Eur. J. **2013**, *19*, 450-455.

Anionic NHC ligands ...
... open new ways for fine-tuning and expanding the coordination chemistry of carbene ligands. Deprotonatio/lithiation of mesoionic 4-arylimino-imidazolium precursors afforded *anionic* NHC ligands bearing a remote anionic amido functionality. The preference for binding to Li^+, $Li(tmeda)^+$, Ag^I and Fe^{II} is examined with respect to the AMIDO-NHC (*i.e.* remote anionic amido – neutral NHC) *vs.* IMINO-IMIDIDE (*i.e.* remote neutral imino–anionic imidazol-2-ylidene-ide) forms. DFT calculations provide insight into the preferred site of the metallation (C_{NHC} *vs.* N_{exo}). The remote backbone substitution clearly offers a versatile way to develop *novel anionic* NHC ligands.

Using functionalized mesoionic imidazolium salts, novel "'Janus-type' organopotassium complexes have been characterised.



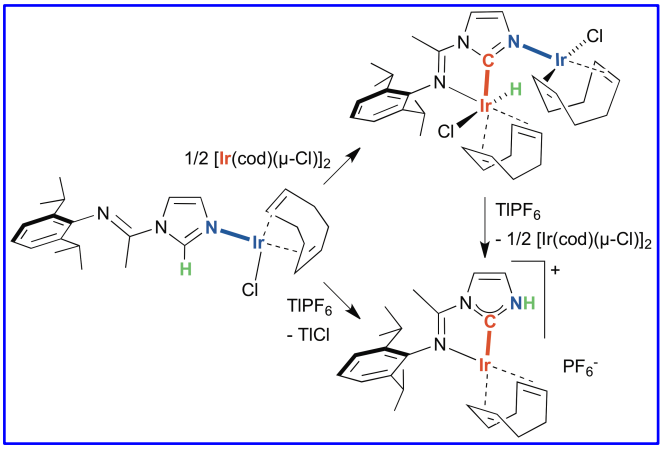
A. A. Danopoulos, P. Braunstein
« Janus-type » Organopotassium Chemistry by Deprotonation of Mesoionic Imidazolium Aminides and Amino N-Heterocyclic Carbenes: Coordination and Organometallic Polymers
Chem. Commun. **2014**, *50*, 3055-3057.

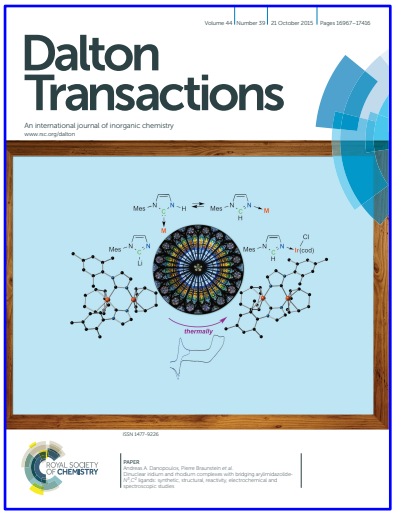
Deprotonation of the observable tautomeric equilibrium mixture of mesoionic 4-aminide imidazoliums and the corresponding 4-amino NHCs allows isolation of a monomeric potassium (imidazol-2-ylidenyl)(anilide), a *'free' anionic* carbene, or polymeric organometallics with 'Janus-type' anionic NHC repeat units.

Of relevance to organic synthesis was the finding that unexpected and unprecedented directed remote lateral lithiation at one $CH(CH_3)_2$ of the 3-(2,6-di-isopropylphenyl) wingtip took place upon the reaction of functionalised N-heterocyclic carbene-type molecules with an excess of $LiCH_2SiMe_3$, leading to dilithiated dianionic 4-amido-N-heterocyclic carbenes. DFT calculations showed that the nature of the isolated species is under thermodynamic control.

A. A. Danopoulos*, P. Braunstein*, E. Rezabal, G. Frison. Unprecedented directed lateral lithiations of tertiary carbons on NHC platforms
Chem. Commun. **2015**, *51*, 3049-3052.

With N-arylimine-functionalised **protic NHC** (pNHC), it was possible to obtain Ir(I) and Ir(III) complexes directly from neutral or cationic Ir(I) imidazole complexes using excess $[Ir(cod)(\mu\text{-}Cl)]_2$ or $TlPF_6$, respectively. N-arylimine-functionalised imidazolium salts lead to imidazole or pNHC complexes by competing N-H or C-H bond activation depending on the type of the imidazolium counterion.



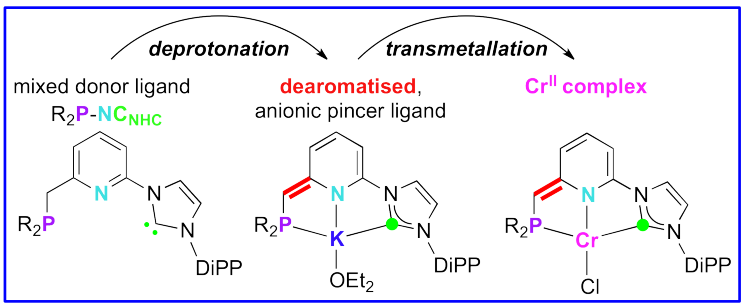


F. He, L. Ruhlmann, J.-P. Gisselbrecht, S. Choua, M. Orio, M. Wesolek, A. A. Danopoulos,* P. Braunstein.*
Dinuclear Iridium and Rhodium Complexes with Bridging Arylimidazolide-N^3,C^2 Ligands: Synthetic, Structural, Reactivity, Electrochemical and Spectroscopic Studies.
Dalton Trans. **2015**, *44*, 17030-17044 (hot paper, cover illustration)

F. He, M. Wesolek, A. A. Danopoulos, P. Braunstein. Homo and Heterodinuclear Ir and Rh Imine-functionalized Protic NHC Complexes: Synthetic, Structural Studies and Tautomerization/ Metallotropism Insights.
Chem. Eur. J. **2016**, *22*, 2658-2671 (inside cover)

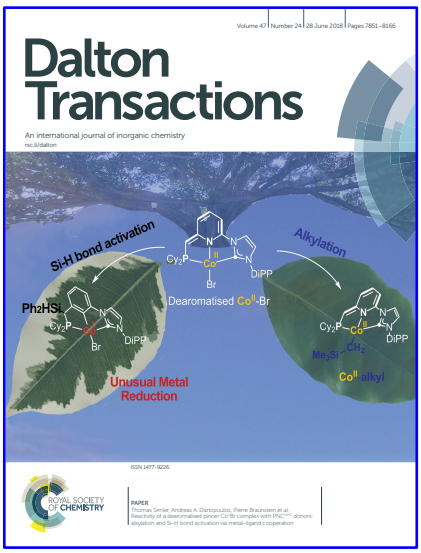
The potentially chelating imino group of imine-functionalized Ir and Rh imidazole complexes influences the formation of functionalized protic NHC (pNHC) complexes by tautomerization/metallotropism sequences. Dinuclear complexes were obtained by double metallation of the azole ring (at both C2 and N3) and a new Rh(I)-Ir(I) heterodinuclear complex was prepared in a stepwise manner, which allowed the chemoselectivity of the synthetic approach to be investigated and understood.

Considering the current general interest in metal-ligand cooperativity in catalytic transformations, an important finding was the deprotonation of the α-picolinyl-CH_2 in the hybrid ligands R_2P-N-C^{NHC} (N = substituted 2-picoline, R = Cy, *t*-Bu; C^{NHC} = *N*-heterocyclic carbene) (L^R) with $KN(SiMe_3)_2$ in ether gave $[KL_{-H}{}^{Cy}(ether)]_2$ featuring a dearomatised picoline backbone. Assisted by 18-crown-6, K^+ dissociation afforded the *Z*- and *E*-isomers of $[L_{-H}{}^R]^-$. Transmetallation of $L_{-H}{}^R$ from $KL_{-H}{}^R$ yielded $[CrCl(L_{-H}{}^{t\text{-}Bu})]$. A major advantage of this method is its versatility.



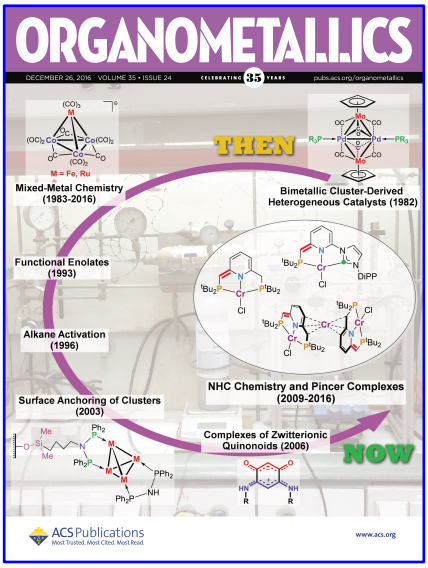
T. Simler, A. A. Danopoulos, P. Braunstein. *N*-Heterocyclic carbene-phosphino-picolines as precursors of anionic 'pincer' ligands with de-aromatised pyridine backbones; transmetallation from potassium to chromium.
Chem. Commun. **2015**, *51*, 10699 10702

Further studies on the reactivity of a dearomatised pincer $Co^{II}Br$ complex with PNC^{NHC} donors allowed alkylation and Si-H bond activation via metal-ligand cooperation



T. Simler, S. Choua, P. Braunstein,* A. A. Danopoulos*. Reactivity of a dearomatised pincer Co^{II}Br complex with PNC^{NHC} donors: alkylation and Si-H bond activation via metal-ligand cooperation.
Dalton Trans. **2018**, *47*, 7888−7895.

On the occasion of the publication of our work on Cr(II) pincer complexes with dearomatised PNP and PNC ligands and their catalytic activity in ethylene oligomerisation, we were invited to provide a cover illustration for *Organometallics* for the 35th anniversary of the journal.

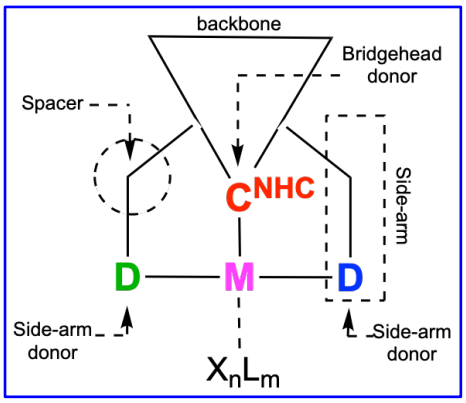


T. Simler, P. Braunstein,* A. A. Danopoulos*. Chromium(II) Pincer Complexes with Dearomatized PNP and PNC Ligands: A Comparative Study of Their Catalytic Ethylene Oligomerization Activity
Organometallics **2016**, *35*, 4044−4049.

A "flash-back" cover for the 35th anniversary of the journal, illustrating some of Braunstein's work published in this journal since its very first issue!

Developing further the concept of underligated metal complexes that is currently attracting considerable international attention, studies were performed on three-coordinate Fe(II) alkyl (*Organometallics*, 2012, *31*, 4102-4105) and [Co{N(SiMe$_3$)$_2$}$_2$L] (L = NHC) complexes (*Organometallics*, 2015, *34*, 2429). Such complexes often display unique catalytic and magnetic properties.

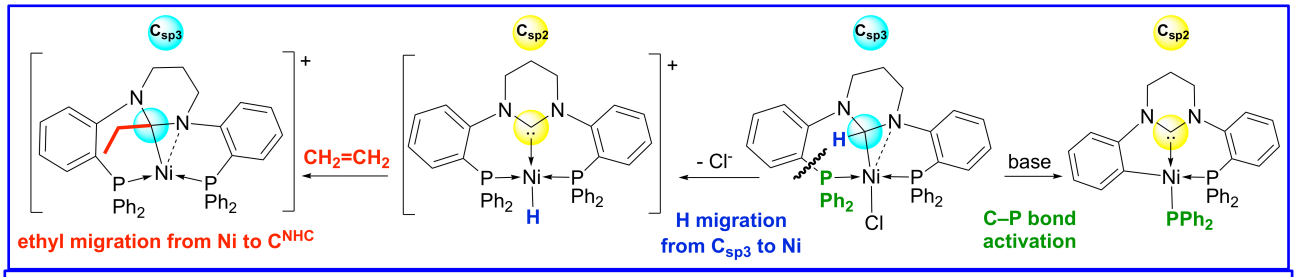
Numerous functional, hybrid NHC ligands have been reported in which additional O, S or P donor functions are associated with one or more NHC donor groups and involved in the bonding to the metal centre(s). This diversity allows fine-tuning of their reactivity and physical properties and it was analysed in review articles. Concerning the very popular class of pincer ligands, a focus was placed on cases where the NHC donor occupies a bridgehead position.



* S. Hameury, P. de Frémont, P. Braunstein. Metal Complexes with Oxygen-Functionalized NHC Ligands: Synthesis and Applications. *Chem. Soc. Rev.* **2017**, *46*, 632-733.
* V. Charra, P. de Frémont, P. Braunstein. Multidentate *N*-heterocyclic carbene complexes of the 3d metals: synthesis, structure, reactivity and catalysis. *Coord. Chem. Rev.* **2017**, *341*, 53-176.
* A. Danopoulos, T. Simler, P. Braunstein**.** *N*-Heterocyclic Carbene Complexes of Copper, Nickel and Cobalt. *Chem. Rev*. **2019**, *119*, 3730-3961.
* F. He, K. P. Zois, D. Tzeli, A. A. Danopoulos, P. Braunstein. *N*-Heterocyclic Carbenes as Bridgehead Donors in Metal Pincer Complexes. *Coord. Chem. Rev*. **2024**, *514*, 215757.

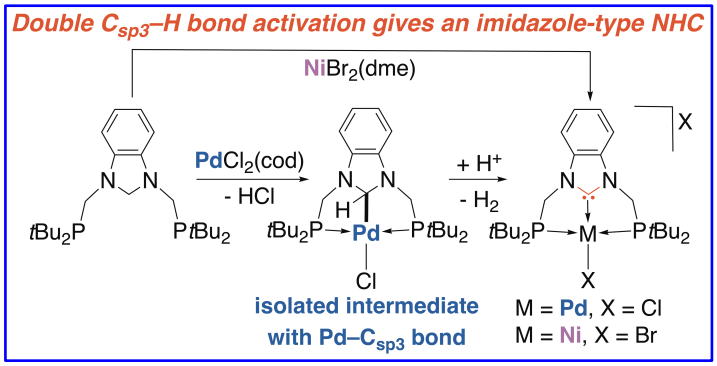
Heterometallic metal chains displaying strong metallophilic interactions supported by double short-bite P-C^{NHC}-P pincer ligands were presented in Section 1.

Unusual chemistry was observed by our group using Ni(II) PCP-Pincer complexes where Csp^3–H and P–C bond activation were observed under mild conditions, while ethylene insertion into a Ni-H bond resulted in very fast ethyl migration from Ni to C^{NHC}. These transformations are highly relevant to several organometallic transformations and reaction intermediates in homogeneous catalysis.



F. He, C. Gourlaouen, H. Pang, P. Braunstein. Influence of the Flexibility of Nickel PCP-Pincer Complexes on C–H and P–C Bond Activation and Ethylene Reactivity: A Combined Experimental and Theoretical Investigation. *Chem. Eur. J*. **2022**, *28*, e202104234 (very important paper).

Furthermore, an unprecedented direct and facile access to Ni(II)- and Pd(II)-imidazole-type NHC ligands was discovered resulting from Ni(II)- or Pd(II)-promoted double geminal $C(sp^3)$–H bond activation in imidazoles.



F. He, C. Gourlaouen, H. Pang, P. Braunstein. Experimental and Theoretical Study of the Ni(II)- and Pd(II)-Promoted Double Geminal $C(sp^3)$–H Bond Activation Providing Facile Access to NHC Pincer Complexes: Isolated Intermediates and Mechanism. *Chem. Eur. J*. **2022**, *28*, e202200507 (hot paper).