Ligand Development

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Synthesis and Coordination Properties of Nitrogen(I)-Based Ligands**

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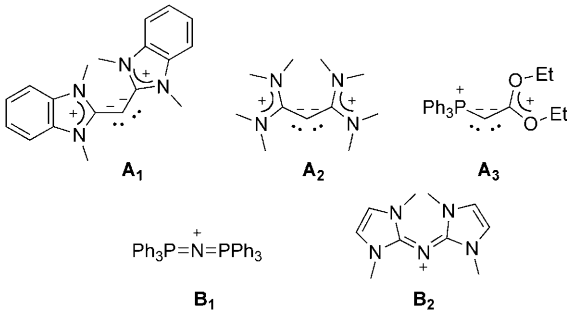
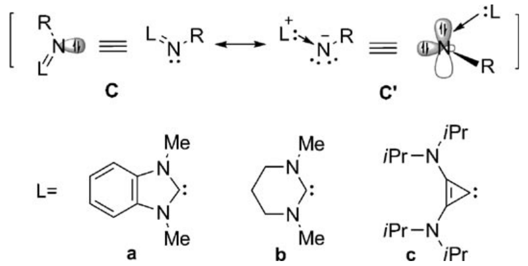
In most organic compounds, nitrogen uses three of its five valence electrons to form bonds with surrounding atoms whilst keeping the other two as a lone pair. Similarly, with the exception of carbon monoxide, carbenes, and isonitriles, carbon is normally tetravalent in organic molecules. However, following seminal work from Ramírez[1] and inspiring theoretical studies from Frenking,[2] Bertrand[3] and Fürstner[4] have synthesized and evaluated the coordination behavior of carbodicarbenes **A_1** and **A_2** and carbophosphinocarbenes **A_3** (Scheme 1). These compounds may be considered as consisting of two carbene ligands, or a carbene and a phosphine, coordinated to a central zerovalent carbon atom.[5]



Scheme 1. Representative structures of carbodicarbenes **A_1** and **A_2**, carbophosphinocarbenes **A_3**, bis(phosphine)iminium cations **B_1**, and bis(carbene)iminium cations **B_2**.

It can be envisaged that this bonding situation can in principle be extrapolated to compounds **B_1** and **B_2**, in which the central carbon atom of carbodiphosphoranes or carbodicarbenes has been formally replaced by an isoelectronic N^+ fragment.[6] However, the positive charge introduced in the systems by such substitution precludes interaction with metal centers. In fact, **B_1** ions have been extensively used as non-interfering cations for the structural characterization of -ate species.[7] A further structural change, directed to retain charge neutrality, is therefore essential.

Replacement of one of the carbene moieties in **B_2** by anionic R^- or Ar^- groups will eliminate the global positive charge yet keep the system isoelectronic with carbodicarbenes. To favor the particular electronic configuration in which the nitrogen atom is able to donate four electrons over that typical of imines, an adequate selection of the ligand L is also crucial. It must be a strong σ donor and at the same time a very poor π acceptor to minimize back-donation from the central nitrogen atom to the carbene moiety (Scheme 2).[8]



Scheme 2. Conceivable resonance extremes of **C**-type imines.

This extreme situation, represented by resonance structure **C′**, may be interpreted as a coordination complex in which a carbene donates two electrons into the empty orbital of a nitrene. The aim herein is to study the synthesis, bonding situation, and coordination properties of compounds of this general structure either to confirm or disprove this view.

The preparation of compounds **3**, **7**, and **11** (Scheme 3) begins with the condensation of readily available chloroiminium species **1** or **5** or chlorocyclopropenium salts[9] **9** with mesitylamine, followed by deprotonation with KH or KHMDS. This route, which is complementary to the one developed by Tamm et al. for the synthesis of imidazoline-2-imines,[10,11] avoids the use of free carbenes; furthermore, it allows the synthesis of compounds of type **Cc** with more structural diversity than previously reported.[12]

The donor ability of these ligands was evaluated by analysis of the CO stretching frequencies for complexes of type $[RhCl(CO)_2\mathbf{C}]$; the data suggest that **3** has a donor capability similar to iminophosphoranes.[13,14] Compound **7** surpasses the strongest electron-releasing N-heterocyclic carbenes, whilst **11** clearly rivals (amino)(ylide) carbene[15] and carbodicarbenes.[3,4b] These exceptional donor properties are highlighted by comparison with other nitrogen-based ligands, such as pyridines or imines.[16]

Especially informative is a comparison between the structures of **10** (see the Supporting Information) and **11** in

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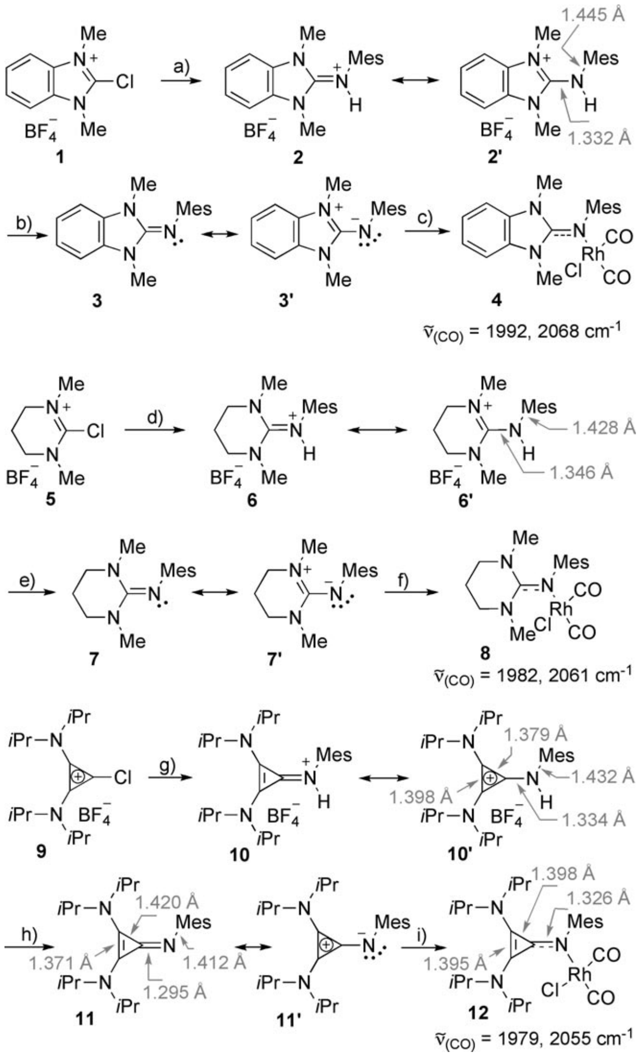


Scheme 3. Reagents and conditions (yields): a) $MesNH_2$, MeCN, 160°C (microwave) 1 h (48%); b) KH, THF, 45°C, overnight (56%); c) $[\{RhCl(CO)_2\}_2]$, THF, 20 min (88%); d) $MesNH_2$, *n*BuLi, THF, reflux, 12 h (78%); e) KHMDS, toluene, $-20°C \rightarrow$ RT (96%); f) $[\{RhCl(CO)_2\}_2]$, THF, 20 min (61%); g) $MesNH_2$, THF, reflux, 24 h (93%); h) KH, THF, 60°C, overnight (91%); i) $[\{RhCl(CO)_2\}_2]$, THF, 20 min (72%). Mes = 2,4,6-trimethylphenyl, KHMDS = potassium hexamethyldisilazide.

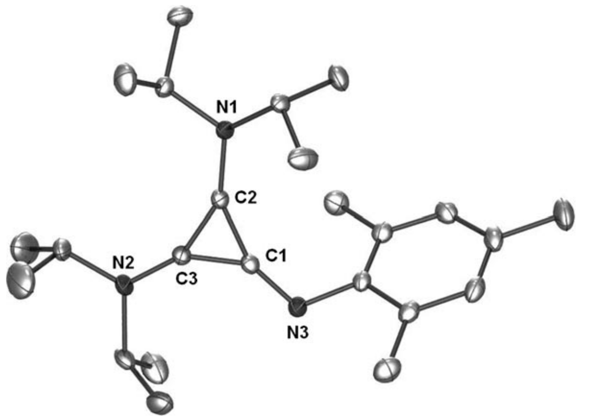


Figure 1. Structure of **11** in the solid state (hydrogen atoms removed for clarity; ellipsoids set at 50% probability).[17]

the solid state (Figure 1). The three C–C bond lengths in the cyclopropenyl ring of **10** are quite similar (1.379–1.398 Å), suggesting that the positive charge largely resides on the aromatic cyclopropenium ring, represented by the mesomeric extreme **10′**. After deprotonation, the structure of **11** indicates, however, that mesomeric form **11′** loses importance. The C1–N3 bond in **11** (1.295 Å) is substantially shorter than in **10** (1.334 Å) and has a typical value for carbon–nitrogen double bonds. Furthermore, the three-membered ring is now less aromatic, with two longer (1.420 and 1.411 Å) and one shorter (1.371 Å) C–C bonds (Scheme 3). Even though these data suggest that the mesomeric structure **11** gains importance in the free ligands, the outstanding donor quality of these compounds can not be explained by considering only its imine character. In fact, the X-ray structure of **12** reveals that, after coordination to rhodium, the cyclopropenyl system regains aromaticity, accompanied by an elongation of the C1–N1 bond (Figure 2).

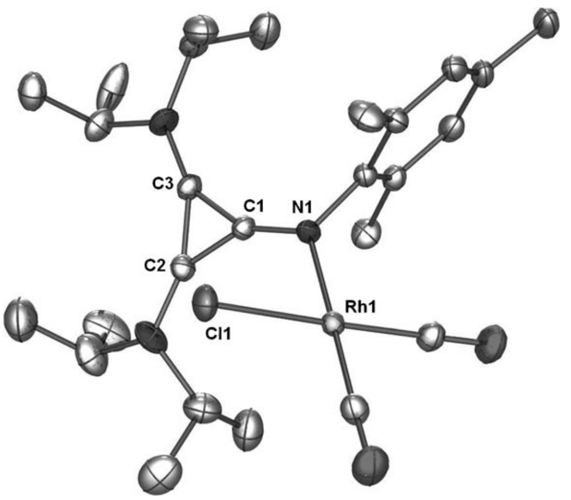
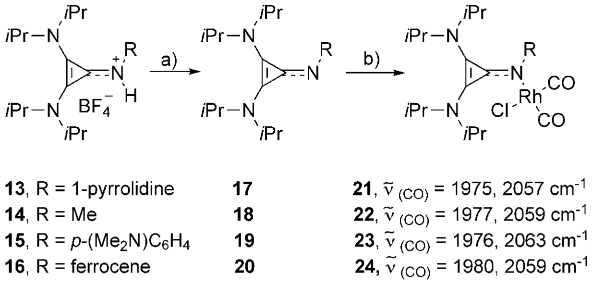


Figure 2. Molecular structure of **12** in the solid state (hydrogen atoms removed for clarity; ellipsoids set at 50% probability).[17]

The cyclopropenyl moiety in these molecules can be thought of as an electron reservoir. In the free ligand, it accepts π electron density from the imino nitrogen, thereby losing some of its aromatic character. Upon coordination it compensates the electron density transferred from the nitrogen atom to the metal, recovering aromaticity. This effect also explains why the total negative charge calculated on the nitrogen atom remains effectively constant, or surprisingly even increases after formation of some gold complexes (see the Supporting Information). The same behavior of the flanking ligands has been previously observed in carbon(0) species.[2,4a]

Once the bis(diisopropylamino)cyclopropenylylidene was identified as the most appropriate carbene to produce extremely electron-rich structures **C′**, the influence of the R group was investigated. Therefore, compounds **17**–**20** were prepared and their electron properties evaluated as previously (Scheme 4). In general, R groups have less influence on the donor ability than the carbene L, and only in the case of the 1-pyrrolidine substituent could a clear albeit small increase of the donor properties be observed.



Scheme 4. Evaluation of the influence of the R groups on ligands of type **C**. Reagents and conditions: a) KH, THF, **17** (92 %), **18** (97 %), **19** (80 %), **20** (93 %); b) $[\{RhCl(CO)_2\}_2]$, THF; **21** (98 %), **22** (72 %), **23** (66 %); **24** (79 %).

In parallel, the bonding situation in compounds **3**, **7**, **11**, and **17**–**20** was evaluated using density functional theory computations at the BP86(RI)/TZVP level. Inspection of the frontier orbitals reveals that in all the cases studied, the HOMO and HOMO−1 correspond to π- and σ-type lone-pair orbitals with maximum coefficients at the central nitrogen atom (Figure 3).

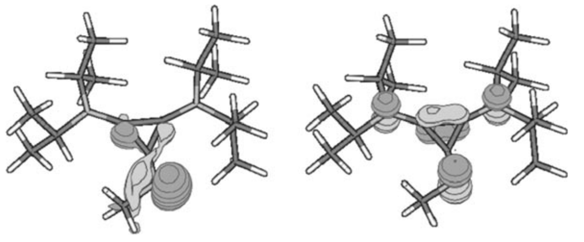
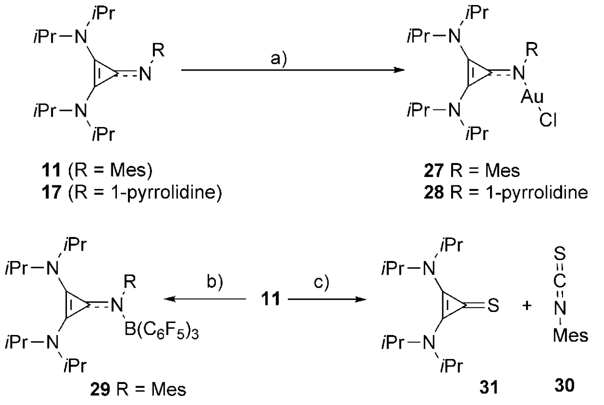


Figure 3. Highest occupied molecular orbitals of **14**: HOMO−1 (left) and HOMO(right).

This finding, together with the calculated first and second proton affinity, support the idea that compounds **11** and **17**–**20** should be considered as nitrogen(I)-containing species. Interestingly, in some cases the energies of the calculated lone-pair orbitals are even higher than those in carbodiphosphoranes or carbodicarbenes, indicating their propensity towards coordination (see the Supporting Information).[2a]

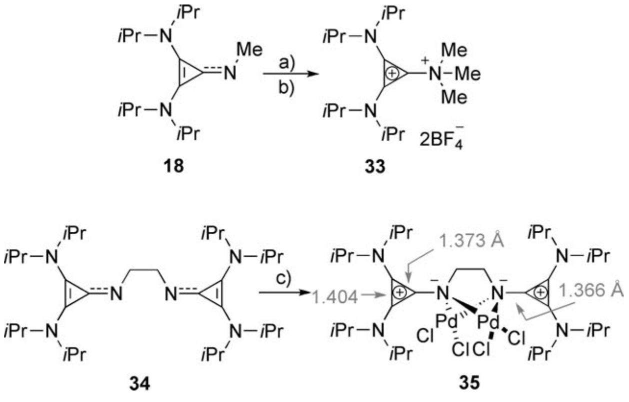
Encouraged by this analysis, the reactivity and coordination properties of these new compounds were studied. Both **11** and **17** react smoothly with soft Lewis acids, such as $[AuCl(Me_2S)]$, affording the desired metal complexes **27** and **28** in good yields (Scheme 5). A hard Lewis acid, such as $B(C_6F_5)_3$, also reacts cleanly with **11** to form the corresponding adduct **29** as colorless crystals (see the Supporting Information). The short B1–N3 bond (1.587 Å)[18] points to an enhanced B–N interaction.



Scheme 5. Reagents and conditions (yields): a) $[AuCl(Me_2S)]$, THF, RT (R = Mes, 76 %; R = 1-pyrrolidine, 84 %); b) $B(C_6F_5)_3$, toluene, RT (72 %); c) CS_2 (3 equiv), THF (quantitative).

Carbodicarbene $\mathbf{A_2}$ reacts with electrophiles such as S_8, CO_2 or CS_2 at the central carbon atom to form zwitterionic adducts.[19] No reaction was observed between **11** and S_8 or CO_2 (1 atm), however, upon addition of CS_2 to a solution of **11**, metathesis of the C=S and C=N bonds takes place yielding a 1:1 mixture of thioisocyanate **30** and thioketone **31** instead of any adduct. This reactivity resembles that of guanidines.[20]

Evidence of whether the central nitrogen atom in these species is a nitrogen(I) is given by the isolation of compounds in which they formally donate two electron pairs. This aim has been achieved herein in two different ways. When **18** was submitted to methylation conditions using an excess of Me_3OBF_4, the dialkylated salt **33** was obtained. Even more interesting, owing to its possible implications in catalysis, is the fact that dimeric structure **34** is able to react with two equivalents of $[PdCl_2(CH_3CN)_2]$. The resulting complex **35** has an unprecedented coordination mode for neutral imine-type ligands in which the central nitrogen atoms donate four electrons each (Scheme 6). The X-ray structure of **35** unequivocally confirms the nitrogen(I) nature of this ligand as predicted by our calculations (Figure 4). Remarkably, despite extensive studies on the coordination chemistry of closely related bis(imidazolin-2-imine) ligands,[21] dimetalation of these compounds has not been achieved.



Scheme 6. Reagents and conditions (yields): a) Me_3OBF_4, CH_2Cl_2, RT (84 %); b) Me_3OBF_4, CH_2Cl_2, reflux (54 %); c) $[PdCl_2(MeCN)_2]$ (2 equiv), THF (21 %).

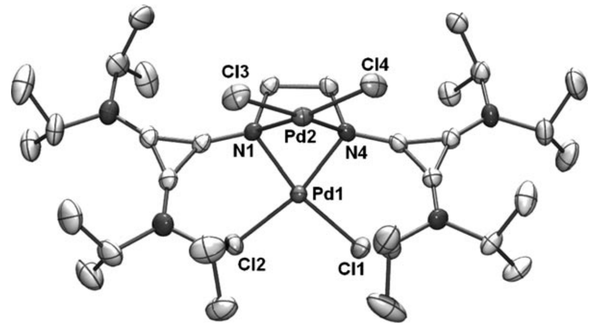


Figure 4. Molecular structure of **35** in the solid state (hydrogen atoms and solvent molecules removed for clarity; ellipsoids set at 50% probability).[17]

In conclusion, the synthesis, bonding situation, and coordination behavior of several highly electron-rich imines, and in particular cyclopropenylylidenimines, has been studied. The central nitrogen atom in these compounds exhibits all the attributes of a nitrogen(I) atom, namely the availability of two lone pairs essentially localized on that atom, and that occupy the HOMO and HOMO−1 orbitals, and the ability to use these electrons in reactions with Lewis acids. The application of these compounds as ligands in homogeneous catalysis is currently under investigation in our laboratory.

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