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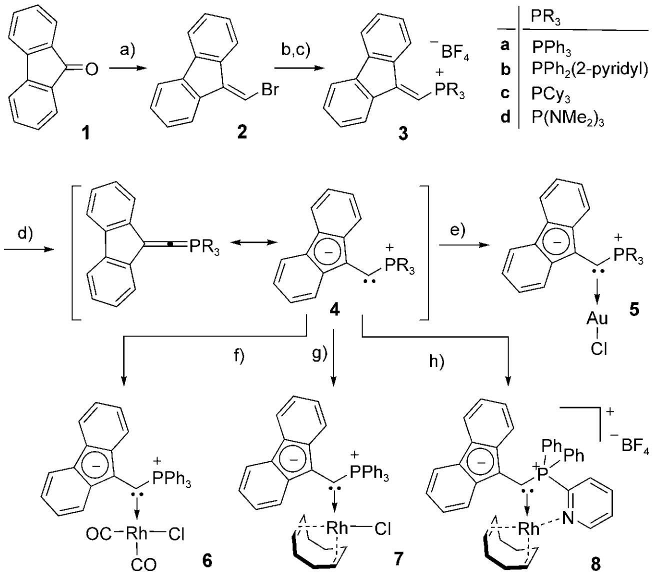
A New Class of Singlet Carbene Ligands

Manuel Alcarazo, Rosa M. Suárez, Richard Goddard, and Alois Fürstner*[a]

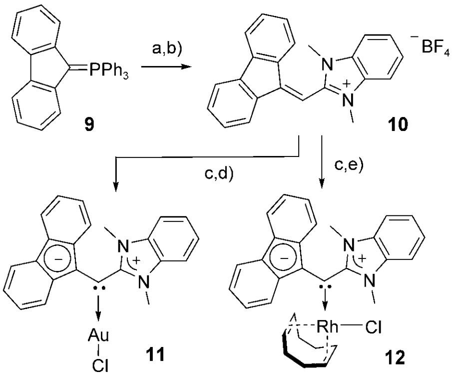
Dedicated to Professor José Barluenga on the occasion of his 70th birthday

Ever since the first isolation,[1] stable carbenes have gained tremendous importance as ancillary ligands for catalytically active transition-metal complexes and as organocatalysts in their own right.[2] To increase the structural range, our group has recently reported the prototype of a new class of singlet carbene ligands.[3] Specifically, deprotonation of the alkenyl phosphonium salt **3a** with potassium hexamethyldisilazide (KHMDS) afforded compound **4a**, which can either be seen as a push–pull cumulene or be described by a zwitterionic resonance extreme owing to the opposing polarization of the two orthogonal double bonds;[4,5] in this representation, the carbene nature of the central C atom becomes clear (Scheme 1).



Scheme 1. a) $Ph_3P{=}CHBr$, THF, −60 °C→RT, 82 %, Ref. [10]; b) R_3P, toluene, reflux; c) $NaBF_4$, MeOH/H_2O, 55 % (**3a**), 68 % (**3b**), 77 % (**3c**), 62 % (**3d**); d) KHMDS, THF, −78 °C; e) [AuCl·SMe_2], 41 % (**5a**), 31 % (**5b**), 19 % (**5c**), 28 % (**5d**); f) [{Rh(CO)$_2$Cl}$_2$], −78 °C→0 °C, 14 %; g) [{Rh(cod)Cl}$_2$], −78 °C→RT, 45 %; h) [{Rh(cod)Cl}$_2$], −78 °C→−20 °C, then $AgBF_4$, −20 °C→0 °C, 55 %.

As part of a program devoted to the synthesis and evaluation of novel carbon-based ligands,[3,6–9] we are committed to explore the scope of this new design principle in more detail. Outlined below are the results of a first round of investigations in which the fluorenyl part of **4** was kept constant but the cationic terminus of the zwitterion was modified. A set of possible precursors was readily attained starting from 9-fluorenone (**1**), which was converted to alkenyl bromide **2** according to a literature procedure (Scheme 1).[10,11] Treatment with various phosphines or HMPA (HMPA = hexamethylphosphoric acid triamide) then gave the corresponding alkenyl phosphonium salts **3a–d** in respectable yields after ion exchange for the less coordinating BF_4^- (for the structures of two such salts in the solid state, see the Supporting Information).[12] Yet another possible carbene precursor **10** was obtained by condensation of the known ylide **9**[13] with commercial 1-methyl-2-formylbenzimidazole and N-methylation of the resulting product with Meerwein salt (Scheme 2).



Scheme 2. a) 1-Methyl-2-formylbenzimidazole, THF, reflux, 80 %; b) $Me_3O{\cdot}BF_4$, CH_2Cl_2, reflux, 98 %; c) KHMDS, THF, −78 °C; d) [AuCl·SMe_2], −78 °C→0 °C, 45 %; e) [{Rh(cod)Cl}$_2$], −78 °C→RT, 28 %.

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[a] Dr. M. Alcarazo, Dr. R. M. Suárez, Dr. R. Goddard,
Prof. A. Fürstner
Max-Planck-Institut für Kohlenforschung
45470 Mülheim/Ruhr (Germany)
Fax: (+49) 208 306 2994
E-mail: fuerstner@kofo.mpg.de

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Deprotonation of **3a** with KHMDS in [D$_8$]THF at −78 °C cleanly generated the reactive intermediate **4a** within 10 min, the central C-atom of which resonates at δ_C= 198.8 ppm. The fact that the corresponding signal of **4d** is even more deshielded (δ_C=214.1 ppm) shows that the nature of the P substituents is intimately correlated with the electronic properties of this site.[14] However, attempts at isolation of either of these species in pure form were unsuccessful.

A low-field signal for the central C atom does not allow the carbene and the cumulene resonance forms of such intermediates to be discriminated; rather, the coordination behavior is thought to be more indicative. Therefore, the corresponding gold and rhodium complexes were targeted, which were obtained on treatment of the respective salt with KHMDS at −78 °C followed by addition of either AuCl•SMe$_2$, [{Rh(CO)$_2$Cl}$_2$] or [{Rh(cod)Cl}$_2$] (cod = 1,5-cyclooctadiene). The greatly different stability of the resulting complexes became apparent upon slow warming of the reaction mixtures. Whereas the metal adducts derived from **3c** and **3d** had to be handled with great care at temperatures ≤ −20 °C under Ar, all other complexes were stable at ambient temperature in air. The gold complex **11** as well as the rhodium complexes **6**, **7**, **8** and **12** could even be purified by flash chromatography over Florisil, although the need for MeOH as a coeluent resulted in some loss of material. Representative examples of the new complexes were characterized by X-ray diffraction (see Figure 1 and 2 and the Supporting Information).[15]

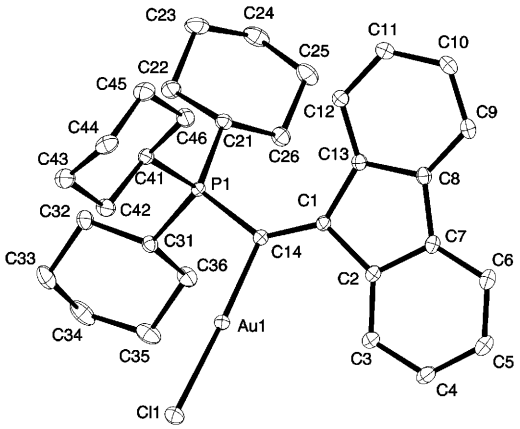


Figure 1. Structure of complex **5c** in the solid state.[15]

In all cases investigated, the metal was bound to the central C atom, which shows the availability of a lone pair at this site and hence the carbene character of the new class of ligands. The conceivable alternative bonding mode, that is, the formation of a cumulene π adduct, makes no noticeable contribution to the ground-state structure of the complexes. The observed C−Au bond lengths (for example, 2.0408(14) Å in **5c**) are similar to those of typical Au−NHC complexes.[16] Allylic strain forces the C−M vector out of coplanarity with the fluorenyl unit, which in turn prevents optimal orbital overlap in the backbone (the angle between the planes defined by the fluorenyl ring and the Au-C-P atoms is 24.39° in **5c**; Figures 1 and 3). A similar distortion may explain why the free carbene of this new push–pull type are less stable than ordinary N-heterocyclic carbenes (NHCs).

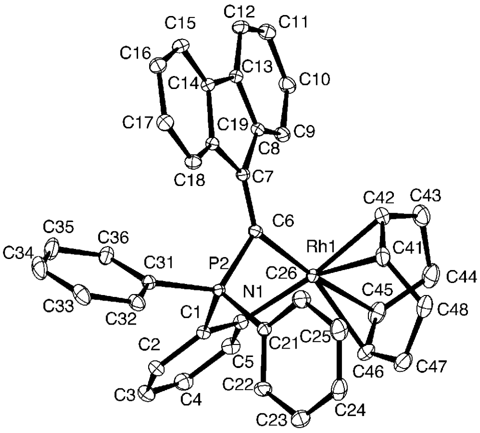


Figure 2. Structure of complex **8** in the solid state.[15] The BF$_4^-$ anion is omitted for clarity.

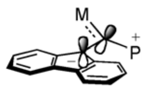
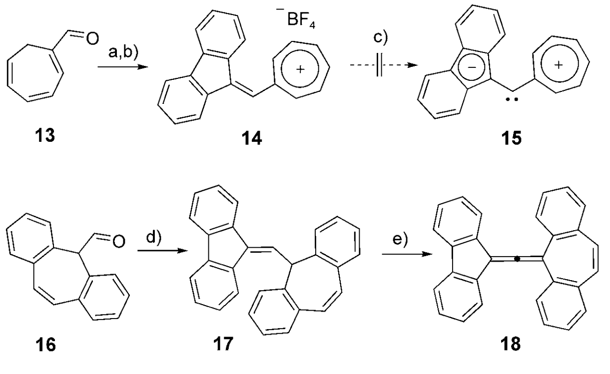


Figure 3. Allylic strain interferes with the optimal orbital overlap within the carbene backbone.

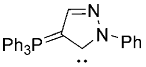
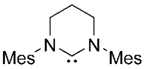
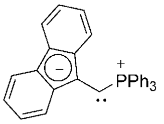
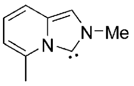
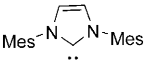
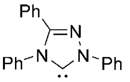
The IR data of the rhodium complex **6** are also quite informative. Frequencies for the unsymmetrical and symmetrical stretching mode of the carbonyl groups at 1979 and 2056 cm^{-1} portray the new carbene ligand **4a** as a powerful donor. As can be seen from the reference data compiled in Table 1, **4a** actually surpasses prototype NHCs in its electron-releasing capacity.

Finally, an attempt was made to extend the concept to the preparation of all-carbon-based singlet carbenes.[21] To this end, the precursor salt **14** and the known olefin **17**[22] were prepared as shown in Scheme 3. Whereas the putative intermediate **15** generated upon deprotonation of **14** decom-



Scheme 3. a) **9**, toluene, 100 °C, 58 %; b) [Ph$_3$C][BF$_4$], CH$_2$Cl$_2$, 0 °C, 75 %; c) KHMDS, THF, −78 °C; d) **9**, toluene, reflux, 73 %; e) DDQ, toluene, 13 %, 90 °C, see Ref. [22].

Table 1. Comparison of carbonyl stretching frequencies in complexes of type $[L\rightarrow Rh(CO)_2Cl]$ in the solid state, which incorporate commonly used singlet carbene donor ligands L [$\tilde{\nu}$ in cm^{-1}].

L	$\tilde{\nu}_{asymm}$	$\tilde{\nu}_{symm}$	Reference
	1965	2052	[6]
	1976	2072	[17]
	1979	2056	this work
	1984	2079	[18]
	1990	2070	[19]
	2009	2089	[20]

posed almost instantaneously even at −78 °C and could not be trapped with $AuCl{\cdot}SMe_2$ either, the corresponding bisbenzo annulated product **18** turned out to be an ordinary allene.[23] As can be seen from Figure 4, unfavorable *peri* interactions combined with allylic strain prevent the seven membered carbocycle from adopting a planar conformation as required for the delocalization of positive charge within this ring. Hence a zwitterionic carbene resonance extreme does not make any substantial contribution to the ground state structure of this particular compound.

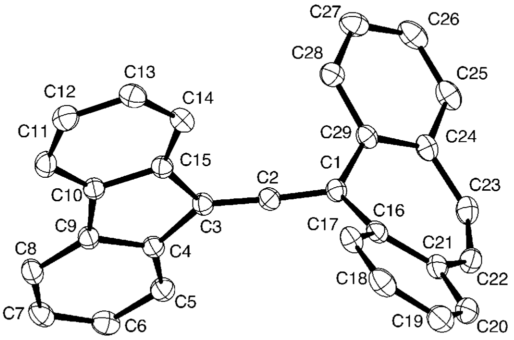


Figure 4. Structure of allene **18** in the solid state.[15]

Although this particular quest for a "stable" all-carbon singlet carbene has not been successful, our results show that the vinyl phosphonium and benzimidazolium salts of the general types **3** and **10** are readily accessible precursors for a new class of singlet carbene ligands endowed with appreciable donor qualities that rival or surpass those of traditional NHCs. Because most of the resulting metal complexes are air and moisture stable, they qualify for applications in catalysis. Investigations along these lines together with further structural variations will be the subject of future reports from this laboratory.

Experimental Section

The entire experimental section, including the characterization of all new substances and the structure of compounds **3b**, **3c**, **5b**, **7**, and **14** in the solid state can be found in the Supporting Information.

Acknowledgements

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Keywords: allenes · carbenes · gold · rhodium · zwitterions

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