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Mini Review

Some aspects of the Lewis base and ligand behavior of *N*-heterocyclic carbenes

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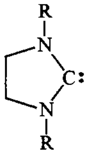
Abstract

The present article is primarily an overview of recent work from the author's laboratory on the chemistry of stable *N*-heterocyclic carbenes. The first section deals with complexes of stable *N*-heterocyclic carbenes with phosphinidenes and arsenidenes, the focal points being preparative methods, molecular structures, electronic structures, and patterns of reactivity. The second section is devoted to complexes of stable *N*-heterocyclic carbenes with d-block metallocenes. Two general approaches have been taken to the preparation of such complexes, namely the direct reaction of stable *N*-heterocyclic carbenes with metallocenes and the reaction of metallocenes with imidazolium chlorides. The molecular structures of several representative complexes have been determined by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbenes; Phosphinidenes; Arsenidenes; Metallocenes

1. Introduction

Almost four decades ago, Wanzlick and co-workers [1] recognized that the stability of *N*-heterocyclic carbenes could be enhanced by the incorporation of α-amino groups (see, e.g. **1**).



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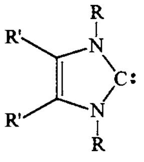

2

Wanzlick et al. [2] also appreciated the possibility that further enhancements in stability could be realized if the carbenic ring featured six π-electrons as in **2**. Indeed, these authors were able to demonstrate the intermediacy of **2** on the basis of trapping experiments. A major breakthrough occurred in 1991 when Arduengo et al. [3] reported the first isolation of a stable, crystalline *N*-heterocyclic carbene **2** (R′ = H; R = adamantyl). As witnessed by the appearance of several recent review articles [4], this important development has stimulated considerable interest in this area of chemistry. New [5] and improved [6] routes to stable nucleophilic carbenes have been reported and many novel structural types, including acyclic systems [7], have been disclosed.

2. Phosphinidene and arsenidene complexes

One of the important generalizations to emerge is that stable *N*-heterocyclic carbenes exhibit a chemical behavior somewhat akin to that of electron rich phosphines. Indeed, it was this aspect that attracted our attention initially. In 1961, Burg and Mahler [8] reported the interesting observation that PMe_3 was sufficiently nucleophilic to disrupt the cyclotetraphosphine, $(PCF_3)_4$, and form the unprecedented phosphine–phosphinidene complex, $Me_3P \rightarrow PCF_3$. A few years later, our group discovered that this complex exhibits fluxional NMR behavior and undergoes exchange by means of a bimolecular process [9]. Given the pro-

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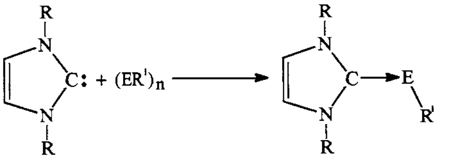
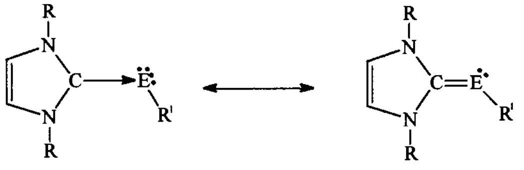
nounced nucleophilicity of carbenes such as **2** (R′ = H; R = mesityl [10]), it seemed plausible that this and related carbenes would also be capable of disrupting homocyclic group 15 systems of the type $(ER)_n$ (E = P, As, Sb) to form products of general formula (carbene)ER.



3: R = Mes; E = P; R′ = Ph; n = 5
4: R = Mes; E = As; R′ = C_6F_5; n = 4
5: R = Mes; E = P; R′ = CF_3; n = 4
6: R = Mes; E = As; R′ = Ph; n = 6

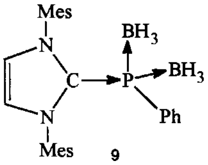
The reactions that are summarized above were carried out in collaboration with Arduengo's group [11].

Two somewhat extreme descriptions can be considered for the electronic structures of the (carbene)ER products as depicted in structures **7** and **8**. Structure **7** represents a phosphinidene or arsenidene complex of a carbene and features a carbon → phosphorus or carbon → arsenic dative bond of order unity while structure **8** corresponds to that of a conventional phosphaalkene or phosphaarsene with a formal C=E double bond. It is of interest to note a parallel with transition metal carbene complexes. Thus the low-valent canonical form **7** resembles a Fischer-type complex, while the high-valent form **8** is reminiscent of a Schrock-type alkylidene complex.



7 (E = P, As) **8** (E = P, As)

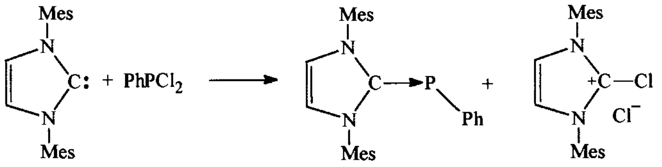
From the structural standpoint, X-ray studies on **3**–**6** revealed that the P–C(carbene) or As–C(carbene) bond distances are ca. 4% longer than those of typical P–C or As–C single bonds. Moreover, it was found that the E–R′ (E = P, As) moiety is displaced from the plane of the carbene ligand by 18–20°. Also, **3** and **5** exhibit upfield ^{31}P-NMR chemical shifts (δ − 23.0 and − 23.6, respectively) which fall well outside the range recorded for typical phosphaalkenes and are suggestive of the transfer of electron density from the carbene to the phosphinidene unit. Collectively, then, the metrical parameters and NMR data imply that the pπ–pπ bond between carbon and phosphorus or carbon and arsenic is very poorly developed and that the electronic structures correspond more closely to structure **7** than to structure **8**. Further proof of this conclusion was forthcoming from Lewis acid-base and electrochemical studies [12]. A conspicuous difference between canonical forms **7** and **8** is that different numbers of lone pairs are present on the E center. It was found that the reaction of **3** with BH_3·thf resulted in the exclusive formation of a bis(borane) adduct, **9**, thus demonstrating the availability of two lone pairs on the phosphorus center. A structural consequence of the attachment of the BH_3 groups to the phosphorus atom is elongation of the P–C(carbene) bond by 0.093 Å and widening of the C–P–C bond angle by 4.9°. Such an increase in bond angle is consistent with valence shell electron pair repulsion theory (VSEPR) in the sense that two lone pairs in **3** are replaced by two bond pairs in **9**.



9

Additional support for the carbene–phosphinidene bonding model (structure **7**) was forthcoming from cyclic voltammetry studies on **3** [12]. Acetonitrile solutions of **3** exhibit a low oxidation potential (− 0.08 V vs. SCE) consonant with an electron-rich phosphorus center. Also, an attempt to assess qualitatively the base strength of **3** was made by treatment of **9** with DBU (1,8-diazabicyclo[5.4.0] undec-7-ene), DBN (1,5-diazabicyclo[4.3.0]non-5-ene), and PAr_3 (Ar = $C_6H_2(OMe)_3$-2,4,6). Both DBU and DBN caused quantitative removal of the BH_3 groups from **9** but PAr_3, the most basic tertiary phosphine known to date (pK_a 11.2) [13], failed to react. The pK_a of **3** is therefore likely to be > 11.2.

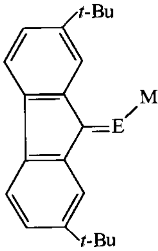
The formation of phosphinidene or arsenidene complexes is not confined to unsaturated carbenes of the general type **2**. Interestingly, a phenylphosphinidene complex of a saturated carbene, **10**, has been prepared by the reaction of **1** with $PhPCl_2$ as shown below [11].



10

This particular procedure avoids the isolation and purification of the corresponding cyclopentaphosphine $(PPh)_5$. Fortunately, the 2-chloro-1,3-dimesitylimidazolinium chloride byproduct is readily separated from **10**. The structure of **10** is very similar to that of **3** apart from twisting about the C4–C5 single bond together with increased pyramidalization at the nitrogen centers.

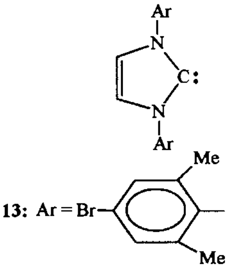
Since fluorenylidene exists as a ground state triplet [14], by analogy with the Schrock-type complexes alluded to above, it would be expected to form double-bonded phosphaalkene and arsaalkene complexes of type **8**. Indeed, it was found [15] that **11** and **12**, which were prepared by sequential LiCl and HCl elimination reactions, feature typical phosphaalkene and arsaalkene C=E double bonds.



11 (E = P); **12** (E = As)

3. Transition metal metallocene complexes

The reactions of *N*-heterocyclic carbenes with lanthanide [16] and main group metallocenes [17] have been described in the recent literature. However, since comparable studies with d-block metallocenes had not been reported when we started our work, this looked like a fruitful area for research. Prior to commencing our studies, we decided to prepare **13**, a new stable carbene, by deprotonation of 1,3-(2,6-dimethyl-4-bromo)imidazolium chloride with KO-*t*-Bu in THF solution.

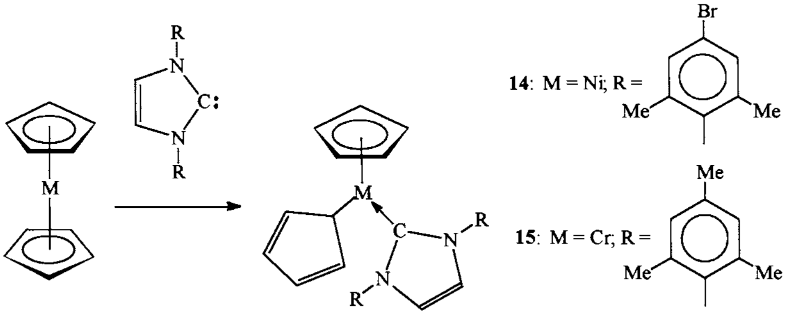


The reaction of **13** with nickelocene in toluene solution at −30°C afforded the deep red, diamagnetic crystalline complex, **14** [18]. Curiously, carbene **13** failed to react with chromocene under comparable conditions. However, reaction did take place with 1,3-dimesitylimidazol-2-ylidene to form a red, paramagnetic crystalline product, **15**, thus implying the sensitivity of carbene reactivity to very subtle structural changes. Multinuclear NMR data for **14**, in concert with mass spectroscopic and analytical data for **14** and **15**, indicated that both products were 1:1 carbene/metallocene complexes (Scheme 1).

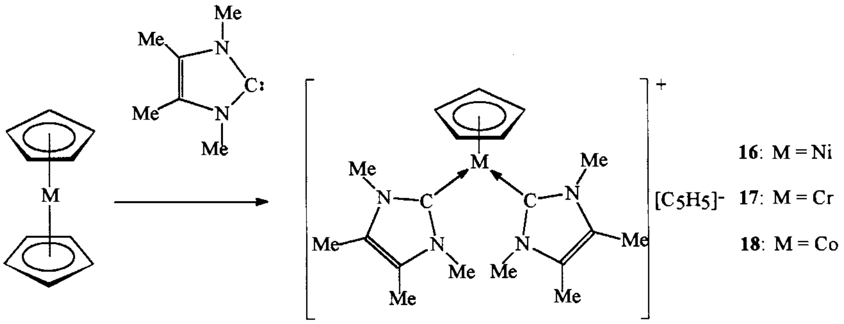
Confirmation was provided by X-ray crystallographic studies which revealed that the coordination spheres of both complexes comprise one η^5-bonded and one η^1-bonded Cp ring along with the η^1-bonded carbene ligand. The Ni–C(carbene) bond length of **14** (1.885(4) Å) is shorter than that reported for the carbene complex, $(\eta^2\text{-}C_2H_4)_2NiC(Ph)NH\text{-}t\text{-}Bu$ (2.008(1) Å) [19] while the Cr–C(carbene) bond length of **15** (2.127(5) Å) is comparable to that of Fischer-type carbene complexes [20]. The principal change that takes place upon coordination of the carbene is twisting of the aryl rings such that steric interactions with the η^5-Cp ligand are minimized. The carbenic carbon–metal–η^1-carbon bond angles are similar for **14** and **15** (95.3(2) and 95.1(2)°, respectively) as are the carbenic carbon–metal–η^5-ring centroid angles (134.9(3) and 128.6(2)°, respectively). A significant feature of the fourteen-electron complex **15** (**14** is an eighteen-electron complex) is that it represents the first example of a thermally stable $(C_5H_5)_2CrL$ species. In previous studies [21] it had been necessary to use intramolecularly bridged Cp ligands to isolate, e.g., a monocarbonyl complex. It is also worth noting that **14** corresponds to an intermediate that has been proposed [22] for the reaction of nickelocene with phosphines.

The less bulky and more nucleophilic carbene tetramethylimidazol-2-ylidene (**2**; R = R′ = Me [5]) causes heterolysis of nickelocene [18], chromocene [18], and cobaltocene [23] to form bis(carbene) complexes of the corresponding $[\eta^5\text{-}C_5H_5M]^+$ fragments along with a cyclopentadienide anion (Scheme 2).

The X-ray crystal structures of **16**–**18** are very similar and in none of the compounds is there evidence of close cation–anion contacts. The geometry at each metal center is trigonal planar within experimental error (using the Cp ring centroids) and the carbene ligands are twisted with respect to the η^5-ring centroid–



Scheme 1.

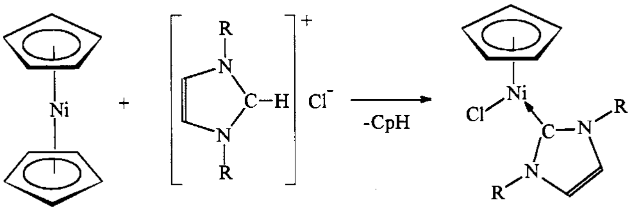


Scheme 2.

M–C(carbene ligands) plane such that the overall cationic geometry is C_2. As expected on the basis of maintenance of the +2 metal oxidation state, the metal–C(carbene) bond lengths in **16** (1.883(2) Å) and **17** (2.097(2) Å) are virtually identical to those in **14** and **15**. It is interesting to note that the heterolytic reaction of nickelocene with stable carbenes contrasts with the insertion reactions that take place with germylenes and stannylenes [24].

An alternative approach to the synthesis of carbene complexes of transition metal metallocenes employs imidazolium salts rather than carbenes as the reagents. Since imidazolium salts are typical precursors for the preparation of stable carbenes, this approach avoids the steps of carbene preparation and purification. While our work in this area was in progress, Tilset and co-workers [25] reported that chromocene reacts with 1,3-dimesitylimidazolium chloride to form the complex $(C_5H_5)CrCl(carbene)$ (**19**). Unfortunately, it was not possible to obtain crystals of **19** suitable for X-ray diffraction. Structural characterization was therefore effected by reaction with PhMgCl which afforded $(C_5H_5)CrPh(carbene)$. We have found that nickelocene undergoes a similar type of reaction with 1,3-dimesitylimidazolium chloride to afford the synthetically useful carbene complex **20** which was amenable to X-ray analysis (Scheme 3).

The molecular structure of **20** features a tricoordinate nickel atom bonded to an η^5-Cp, a carbene, and a chloride ligand. The geometry at nickel is trigonal planar (sum of bond angles is 360.0° using the η^5-Cp ring centroid); however, the bond angles depart significantly from the ideal values, ranging from 98.4(2)° for C(carbene)–Ni–Cl to 132.4(2)° for C(carbene)–Ni–Cp(ring centroid). The Ni–C(carbene) bond length of 1.917(9) Å for **20** is similar to those of **14** (1.885(4) Å) and **16** (1.883(2) Å). Also, the carbene ligand geometries of **20** and **14** are similar in the sense that the mesityl rings are twisted away from the carbene ligand plane in order to minimize steric interactions with the other ligands. Overall, the structure of **20** resembles those of recently prepared ruthenium complexes of the type $(\eta^5\text{-}C_5Me_5)RuCl(carbene)$ [26]. Finally, it is worth noting that the Ni–Cl bond of **20** readily undergoes metathesis reactions with e.g. alkylating agents.



Scheme 3.

4. Conclusions

Stable *N*-heterocyclic carbenes are sufficiently nucleophilic to form 1:1 complexes with phosphinidene (PR) or arsenidene (AsR) moieties. The bonding in such complexes is predominantly of the donor–acceptor type, i.e. (carbene) → ER (E = P, As). Stable *N*-heterocyclic carbenes also react with d-block metallocenes to give either covalent complexes of 1:1 stoichiometry, i.e. $[M(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(carbene)]$ (M = Cr, Ni), or ionic complexes of the genre $[M(\eta^5\text{-}C_5H_5)(carbene)_2][(C_5H_5)]$ (M = Cr, Co, Ni) depending on the type of carbene employed. The reaction of nickelocene with 1,3-dimesitylimidazolium chloride affords the synthetically useful complex, $[Ni(\eta^5\text{-}C_5H_5)(Cl)(carbene)]$.

Acknowledgements

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