Review

Contributions to the chemistry of carbenemetal chemistry

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Abstract

This paper provides a brief review of our researches on carbenemetal complexes. The main emphasis is on saturated heterocyclic bis(amino)carbene ligands, referred to here as electron-rich olefin- or ERO-derived ligands, as outlined in Sections 2 and 3. The following Section deals with Fischer-type carbene complexes, based on reactions of a transition metal substrate with an imidoyl chloride, Vilsmeyer reagent or Eschenmoser salt. The researches of Sections 2, 3, 4 have resulted in the synthesis, characterisation and selected reactions (including as catalysts) of carbene complexes of V, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt and Au in various oxidation states. A final Section describes some more recent work on $C[(NCH_2Bu^t)_2C_6H_4{-}1,2]$, its adducts with $M[(NCH_2Bu^t)_2C_6H_4{-}1,2]$ (M = Si, Ge, Sn, or Pb) and the biphenyl- bis(carbene), $[C\{NCH_2Bu^t\}_2C_6H_3{-}3,4]_2$.

## Contents

1. Introduction

Our group was the first to prepare carbenemetal complexes from an enetetramine (an electron-rich olefin or ERO) such as **1** [1] or a Vilsmeyer reagent such as **2** [2]; we provided the first model system demonstrating that a carbenemetal complex was implicated in an (ERO) olefin metathesis [3], and showed that EROs were then a new class of benzoin condensation catalysts (cf. vitamin B_1) [4]. Such studies on carbenemetal complexes and related chemistry were particularly vigorously pursued in the period 1971 (cf. the first publication [5]) to 1985. We reviewed transition metal carbene complexes in 1972 [6], their role as reaction intermediates in 1973 [7], optically active EROs and their metal complexes in asymmetric synthesis and catalysis in 1981 [8], and the coordination chemistry of nucleophilic carbenes (and dialkylstannylenes) in 1975 [9] and

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of EROs in 1988 [10]. Our work on carbenemetal complexes in the latter review [10] referred to about 500 such complexes described in 35 full papers [11,12], 3 reviews [6,7,9] and 25 preliminary communications. Subsequent such papers are listed in [13].

1 (abbreviated as L^{Me}_2)   **2** (X = H, Cl, or NMe$_2$)
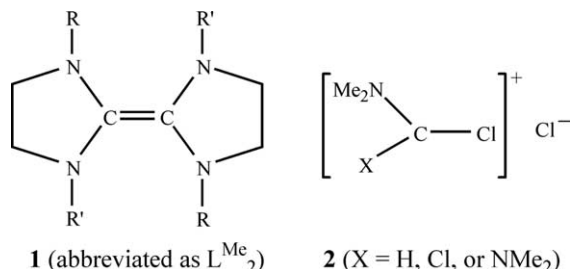
The aim of this paper is to provide a short resumé of some of our contributions to the chemistry of metal complexes having one or more saturated carbene ligand such as **3** or **4**, and finally to describe more recent research on the unsaturated analogues **5** and **6**.
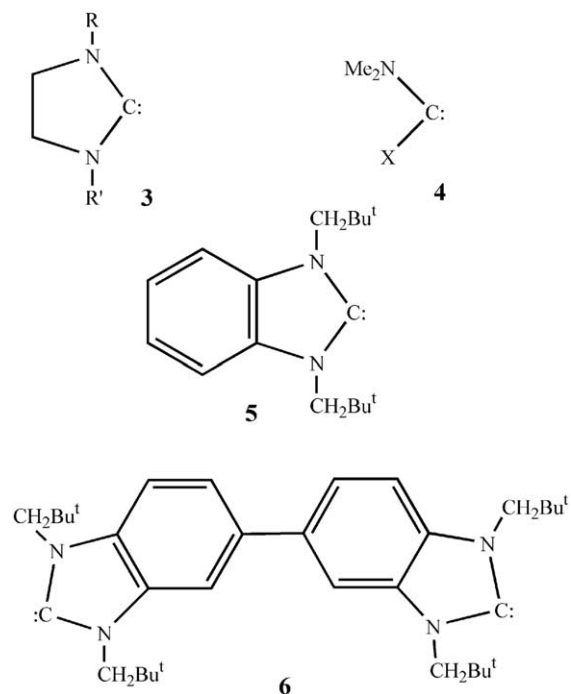

2. Synthesis of ERO-derived transition metal carbene complexes

Well characterised complexes having 1, 2, 3 or 4 carbene ligands of Cr^0, Cr^I, Mo^0, Mo^{II}, W^0, W^{II}, Mn^I, Fe^{-II}, Fe^0, Fe^I, Fe^{II}, Ru^{-II}, Ru^0, Ru^{II}, Os^{II}, Co^{-I}, Co^{II}, Co^{III}, Rh^I, Rh^{III}, Ir^I, Ir^{III}, Ni^0, Ni^I, Ni^{II}, Pd^{II}, Pt^{II}, Au^I

and Hg^{II} have been prepared from an ERO of type **1** by: (a) di-μ-Cl- or di-μ-Br-dimetal bridge-splitting (Rh, Pd, Pt); (b) displacement of a neutral (CO, PR$_3$, or alkene) or (c) an anionic (e.g., Cl$^-$) ligand. These procedures are illustrated by the examples of Scheme 1 [10]. Such complexes have been neutral or cationic (as in Scheme 1) [12]. The only case of a chelating bis(carbene) ligand was in the cation of [*cis*-Rh(COD)(L_2^{cyclam})][RhCl$_2$-(CO)$_2$-*cis*] (**7**), obtained from the ERO **8** (derived from cyclam) and successively [{Rh(COD)(μ-Cl)}$_2$] and CO, illustrated in Fig. 1 [14]. Complexes **9** (or analogues) and **10** (or analogous low spin d^7 compounds) were the first paramagnetic carbenemetal complexes to be stable at ambient temperature [15].

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$[Cr(CO)(DMPE)_2(L^{Me})][BF_4]$
9

$[Fe(CO)(L^{Me})\{P(OPh)_3\}_3][BF_4]$
10
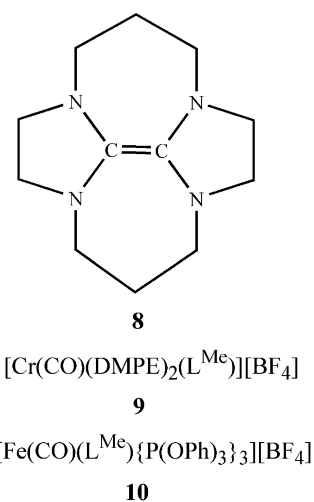
A limitation of the ERO-based synthesis of carbenemetal complexes from an ERO is that EROs are only accessible with primary alkyl or unhindered aryl (these
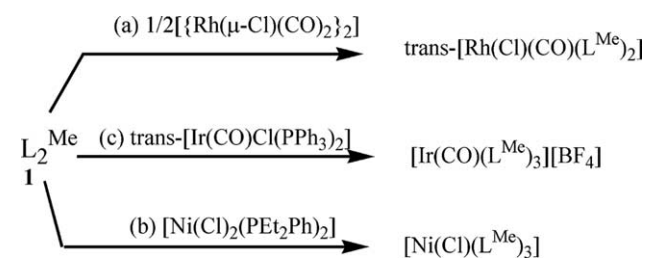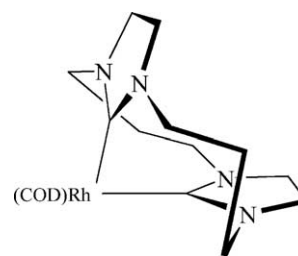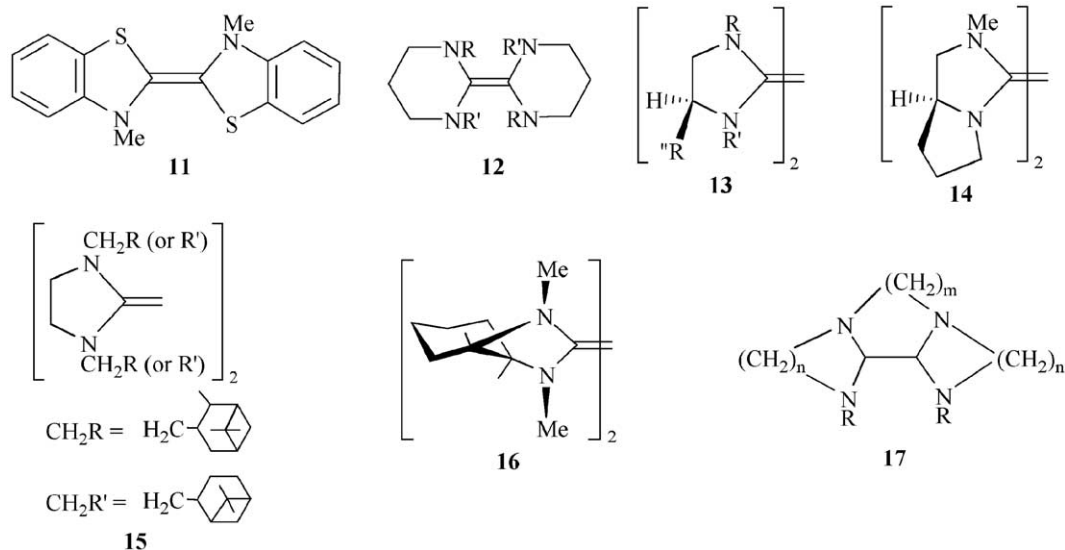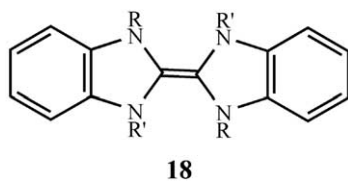

Scheme 1.

Fig. 1. Representation of part of the molecular structure of the cation **7** [14]; the C–Rh–C angle is 78.1°.

are less reactive) substituents at the nitrogen atoms. Examples of skeletal arrangements of such EROs, other than those shown in **1** or **8**, are illustrated in **11–17**. Optically active EROs **13–16** were obtained by syntheses based on the appropriate S-amino-acid (**13–15**) or R-(−)-trans-1,2-diaminocyclohexane (**16**) [16].

the presence of a Rh^I complex as catalyst a statistical mixture of L_2^{Ph}, L_2^{Tol-p} and 2 L^{Ph}–L^{Tol-p} was obtained. This led to the proposal of the model alkene metathesis catalytic cycle of Scheme 4 [3]. Thus, (independently of the work of Hérrison and Chauvin [21]), this led us to propose that alkene metathesis implicates both carbene-metal and metallacyclobutanes in the catalytic cycle [3].

The general routes to the EROs **1** which we have used are summarised in Scheme 2. The procedure most widely employed was that of a modification of step (i) of Scheme 1 [17]. The pathway of step (ii) is exemplified by the synthesis of **18** from 1,3-dimethylbenzimidazolium iodide and NaH [13g].


Scheme 3 shows the proposed reaction pathway from an ERO to a carbenemetal complex, exemplified by the formation of $[M(CO)_5(L^R)]$ from $[M(CO)_6]$ and L_2^R (M = Cr, Mo or W) [18]. The alternative, of predissociation of the ERO to generate the free carbene of type **1**, was discounted (but see [19]), since mixing L_2^{Ph} and L_2^{Tol-p} did not result in redistribution [20]; but in

3. Structures, bonding and reactivity of ERO-derived transition metal carbene complexes

Spectroscopic data of diagnostic value for characterising ERO-derived transition metal carbene complexes include the $v_{asym}(CN_2)$ IR band at 1480–1520 cm^{-1} and the ^{13}C NMR shift for C_{carb} at 200–230 ppm [10]. Variable temperature ^1H NMR spectral experiments on a number of such complexes showed that there is restricted rotation about the M⇋C bond with typical activation free energies of 40–60 kJ mol^{-1}. From He(I) photoelectron spectra (PES), the first ionisation potentials of $[M(CO)_5(L^{Et})]$ and $[Fe(CO)_4(L^{Me})]$ were found at 7.12 (Cr), 6.90 (Mo), 7.02 (W) and 7.3 (Fe) eV [10]; the first six PES bands for $[Fe(CO)_4L]$ [L = $\overline{CN(Me)CH}$=CHNMe or $\overline{CO(CMe_2)_2O}$] were assigned with the aid of MO calculations [22], which confirmed the view [23] that each of the carbene ligand is a good σ-donor but weak π-acceptor, rather like a tertiary phosphine. X-ray data on numerous complexes, including
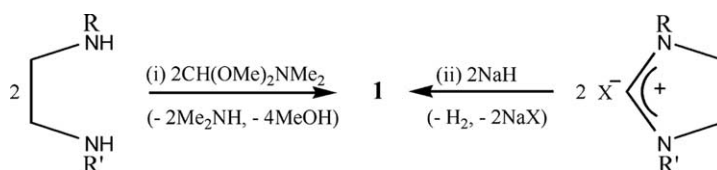

Scheme 2.

Scheme 3.

Scheme 4.
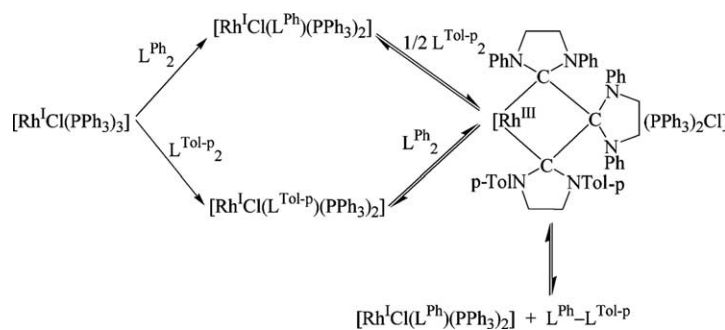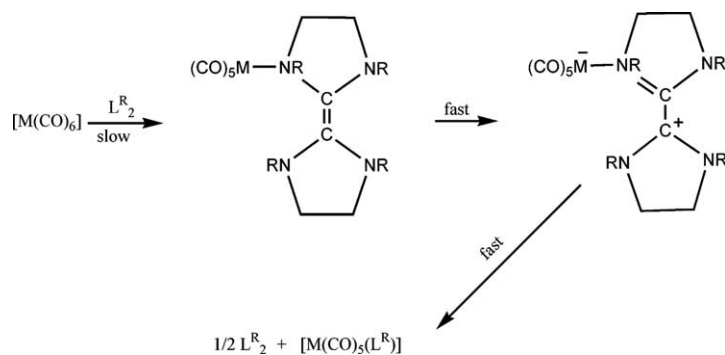
cis- and *trans*-[PtCl$_2$(L^{Ph})(PEt$_3$)], showed that the M–C$_{carb}$ bond is not particularly short and hence has little π-character. From such results on Pt^{II} complexes, it was established that the *trans*-influence for various ligands decreased in the sequence L^R ≈ PR$_3$ > Cl$^-$, also consistent with the view that the ERO-derived carbene ligand is a good σ-donor but poor π-acceptor.

It is often held, but see [24], that a useful distinction can be made between a Fischer-type and Schrock-type carbenemetal complex, such as [Cr(CO)$_5${C(OMe)Ph}] and [Ta(CH$_2$Bu^t)$_3${C(H)Bu^t}], being susceptible to nucleophilic and electrophilic attack at C$_{carb}$, respectively. Although L^R ligands such as **3** are nucleophilic carbenes, ERO-derived carbenemetal complexes differ from both, in that the coordinated ligands are resistant to either type of attack at C$_{carb}$. It is this inertness, coupled to firm M-C$_{carb}$ binding, that makes L^R valuable spectator ligands, a property now very widely exploited in catalysis.

A carbene ligand is generally not readily displaced from an ERO-derived carbenemetal complex. However, steric effects may provide exceptions, as in the thermal conversion of *trans*-[RuCl$_2$(L^{Me})$_4$] into [RuCl$_2$(L^{Me})$_3$] [25]. Reactions at metal centres of such complexes include oxidations (e.g., Fe^0 → Fe^I), oxidative additions, e.g., *cis*-[Mo(CO)$_4$(L^{Et})$_2$] → [MoBr$_2$(CO)$_2$(L^{Et})$_2$], isomerisations, e.g., *cis*- ⇌ *trans*-[W(CO)$_4$(L^{Et})$_2$], or dehy-

drochlorinative cyclometallation and its retrogression as in [Ir(L^{Tol-p})$_2$(L^{Tol-p})]Cl $\overset{-HCl}{\underset{HCl}{\rightleftharpoons}}$ [Ir(L^{Tol-p})$_3$] [for Ir(L^{Tol-p}), see **19**] [26].
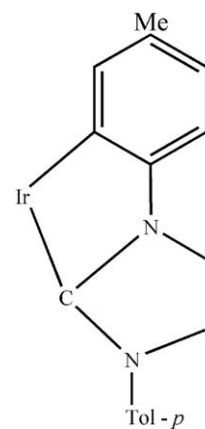
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ERO-based carbenemetal complexes were shown to be effective homogeneous catalysts, with an activity similar to those of tertiary phosphine analogues for: (a) *hydrogenation* of an *N*-acylamido acrylic ester (e.g., using [RuCl$_2$(L^{Me})(PPh$_3$)$_2$]), (b) *hydrosilylation* of an alkene, alkyne or ketone, e.g., using *cis*-[RhCl(COD)(L^{Me})], (c) *cis*- ⇌ *trans-isomerisation* of

PhCH $=$ C(H)SiEt$_3$ using *trans*-[RhCl(L^{Me})(PPh$_3$)$_2$], (d) *Si–Si-coupling* (e.g., SiH$_2$Ph$_2$ $\rightarrow$ [Si(H)Ph$_2$]$_2$) using *cis*-[RhCl(COD)(L^{Me})], (e) the *metathesis* of L$_2^{Ph}$ + L$_2^{Tol-p}$ $\rightleftharpoons$ 2L^{Ph}-L^{Tol-p} (using a Rh^I complex), (f) the *metathesis* of *c*-C$_6$H$_{10}$ + C$_2$H$_4$ using [Mo(CO)$_5$-(L^{Me})] with AlCl$_2$Et/[NBu$_4$]Cl, and (g) the *polymerisation* of CH$_2$ $=$ C(Me)CO$_2$Me using *cis*-[M(CO)$_4$(L^{Me})$_2$] (M $=$ Cr, Mo or W); for (a)–(e), and (f) and (g), see [10] and [27], respectively.

## 4. Fischer-type transition metal carbene complexes

Our experiments in this area are quite distinct from those pioneered by Fischer, being based on carbenoids as precursors: imidoyl chlorides, Vilsmeyer reagents or an Eschenmoser salt. The work was triggered by the discovery in 1972 that a chlororhodium(I) complex with various imidoyl chlorides gave carbenerhodium(III) trichlorides (Scheme 5; e.g., L $=$ (CO)$_2$ and L' $=$ CO), a process then designated as a "three-fragment oxidation addition" [28].

The tandem imidoyl chloride/HCl route led to syntheses based on [R$_2$NC(H)Cl]Cl (R $=$ Me, Et, Pr^i or Bu; or bromide analogues) or [Me$_2$NCCl$_2$]Cl as the carbenoid. By the three-fragment oxidative addition, various carbenerhodium(III) chlorides were prepared [9]; alternatively, related complexes were accessible by a salt elimination, e.g. [Cr(CO)$_5${C(Cl)NMe$_2$}], from Na$_2$[Cr(CO)$_5$] and [Me$_2$NCCl$_2$]Cl. Such a chlorocarbene complex with various silver salts provided a new route to carbynemetal complexes, e.g. [Cr(CO)$_5$(CNMe$_2$)][BF$_4$] [29]. From [Me$_2$NC(H)Cl]Cl alternative routes (i)–(iii) to the first *secondary carbenemetal* complexes were developed: (i) the three-fragment oxidative addition procedure gave a series of Ru^{II}, Rh^{III}, Ir^{III} and Pt^{II} complexes; (ii) a salt elimination pathway yielded V^I, Cr^0, Mo^0, W^0 and Fe^0 complexes; and (iii) a salt elimination with concomitant oxidative addition led to Mo^{II}, W^{II}, Mn^I, Re^I and Co^I analogues; these routes are exemplified in Scheme 6 [30].

5. Studies on Arduengo-type carbenes and derived metal complexes

Our researches in this area were part of a wider programme, namely that of robust, crystalline bis(amino)metallene(II)s, E(NR$_2$)$_2$ (E $=$ C, Si, Ge, Sn or Pb), including their role as ligands, which commenced in 1971; results on carbenemetal complexes were described, in outline, in the preceding Sections 1–4. Subsequently there followed reports on the first stable monomeric group 14 bis(amino)metallenes such as E[N(SiMe$_3$)$_2$]$_2$ (E $=$ Ge, Sn, or Pb) [10,31] and
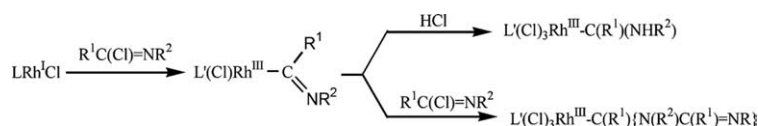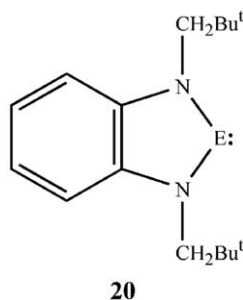

Scheme 5.
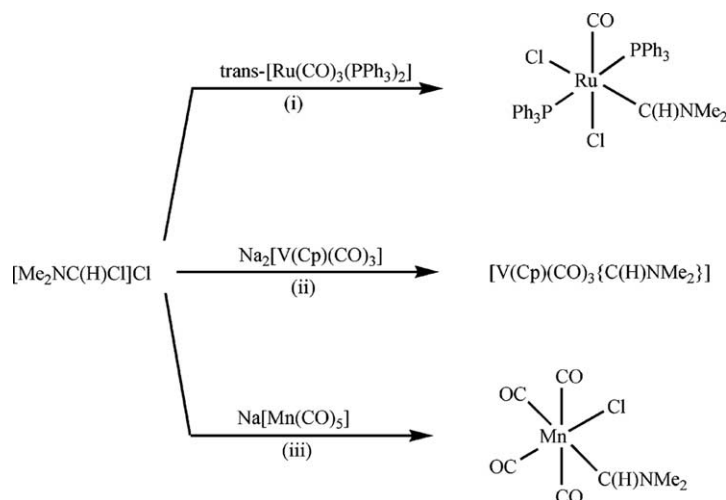
Scheme 6.

(much later) by the monomeric silylene **20** [E = Si, abbreviated as Si(NN)] [31,32] and their transition metal complexes.

20

The crystalline, monomeric carbene **20** (E = C; C(NN)) was prepared [33] (and independently by Hahn et al. [34]) by reduction of the thiourea S = C(NN) with KC$_8$ in THF. Treatment of [Ni(COD)$_2$] with this carbene yielded the carbenemetal(O) complex [Ni{C(NN)}$_2$] [33]. From the latter and Si(NN), the carbene-silylene adduct **21** (M = Si) was obtained, also accessible from C(NN) + Si(NN); the X-ray structure of **21** (M = Si) showed that the sum of the bond angles subtended at C$_{Carb}$ was 351.4° (i.e., approaching planarity) and 291.6° at Si (i.e., close to pyramidicity at Si) with a rather long C–Si bond [33]. DFT calculations on model carbenesilylene adducts were consistent with the C$^+$–Si$^-$ bond polarity in the 1:1-adduct [33]. The study was extended to the wider series of carbene adducts of group 14 metallenes **21** (M = Si, Ge, Sn, or Pb); the X-ray structures of each of these crystalline complexes, as well as variable temperature ^{x}M and ^{13}C NMR spectra (^{29}Si, ^{119}Sn, ^{207}Pb = ^{x}M) for toluene-d_8 solutions, were recorded [35]. The latter data showed that each adduct readily dissociated in solution, its stability decreasing in the sequence M = Sn > Pb > Si > Ge. From the magnitude of the chemical shifts, their conformation (Fig. 2) and the long C–M distances
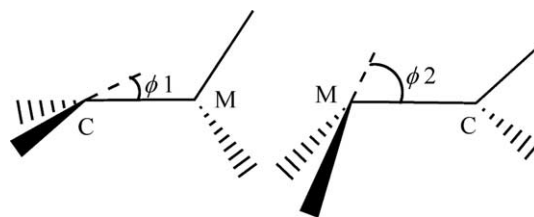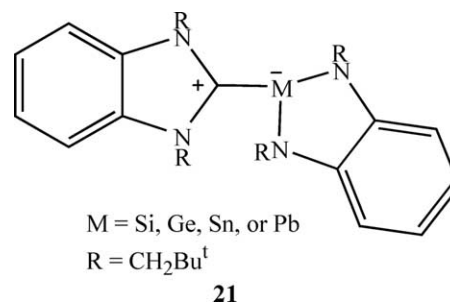

Fig. 2. Sketches illustrating the fold angles $\phi1$ and $\phi2$ of **21**.

Table 1
Comparative C–M bond lengths (Å) and bond angles at C and M of **21**

Complex	C–M (Å)	$\phi1$ (°)[a]	$\phi2$ (°)[a]	Ref.
(NN)CSi(NN)	2.162(5)	28	77	[33]
(NN)CGe(NN)	2.339(3)	31	75	[35]
(NN)CSn(NN)	2.472(5)	27	79	[35]
(NN)CPb(NN)	2.586(7)	28	80	[35]

[a] $\phi1$ and $\phi2$ are defined in Fig. 2.

M = Si, Ge, Sn, or Pb
R = CH$_2$Bu^t

21

Following the discovery of stable *N*-heterocyclic bis(amino)carbenes, a wide range of modifications has been made to extend the range of such compounds. Some of these involved the linking of two bis(amino)carbene moieties through nitrogen atoms with a linker group (see [36]). A different approach has recently been reported by us, whereby the two carbene moieties of type **20** (E = C) were linked at the carbon backbone leading to the biphenyl-biscarbene **22**, eqn (1) (R = CH$_2$Bu^t) [36].

(1)

22
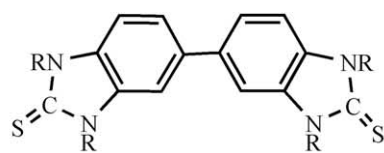
in **21** (ca. 10% longer than for a typical M^{II}–C bond in an MR$_2$ molecule), it was concluded that the C—M bond in each adduct is best formulated as being electrostatic in nature, with the carbene moiety as the electron-donor and the M(NN) fragment as acceptor. Some structural data are summarised in Table 1.

Acknowledgments

ligands, referred to herein as ERO-derived carbenes, have been the forerunners of much important work by others, including those described elsewhere in this volume. Did we leave the field too early? Perhaps, but then you cannot win them all!

I owe a great debt to the talented coworkers whose names appear in the references. It has been a pleasure and privilege to work with them and enjoy their friendship. I am grateful to Dr. A.V. Protchenko for help with the manuscript.

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