Reactivity of Terminal Transition Metal Borylene Complexes

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ABSTRACT: *The chemistry of terminal transition metal borylene complexes is reviewed, with particular attention to recent developments concerning the reactivity of these species.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:566–571, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20143

INTRODUCTION

Transition metal carbonyls constitute one of the most prominent classes of organometallic compounds, displaying a wealth of structural complexity and chemical reactivity. Carbonyl complexes are ubiquitous in organometallic chemistry and homogeneous catalysis, for reasons that relate to the experimental accessibility of CO and its efficient, synergic binding to transition metals. The quest for molecules that would display similar properties has identified borylenes, B─R, as excellent candidates [1–3]. However, the known instability and consequent high reactivity of borylenes as free molecules [4] mean that transition metal borylene complexes are challenging targets of long standing for synthetic chemists [5─11]. During the past 15 years, renewed interest in the chemistry of transition metal complexes of boron made possible, for the first time, to generate and stabilize borylenes in the coordination sphere of various transition metals. Species where the borylene

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unit adopts a bridging position between two metals represent the most numerous and well-studied class of compounds [12–20]. Appropriate synthetic routes to their terminal counterparts were developed more recently [21–27]. However, significant limitations affect the preparative protocols that lead to terminal borylene species, a fact that partly undermines the possibility to study the reactivity of such compounds. Nonetheless, a number of interesting findings concerning the chemical properties of terminally bound borylene units have been recently reported and these will constitute the subject of the present review article.

SYNTHESIS OF TRANSITION METAL TERMINAL BORYLENE COMPLEXES

The most general approach to the synthesis of transition metal terminal borylene complexes is based on the action of dianionic carbonylates on suitable dihaloboranes. The resulting double salt-elimination reaction generates species such as $[(OC)_4Fe\text{─}B(\eta^5\text{-}C_5Me_5)]$ (**1**) and $[(OC)_5M=BN(SiMe_3)_2]$ (M = Cr, **2**; M = W, **3**), first reported by Cowley et al. [28] and Braunschweig et al. [21], respectively, in 1998 (Fig. 1).

A common feature of compounds **1–3** is the presence of sterically demanding and electron-releasing substituents at boron, a requisite that, according to theoretical calculations, is necessary to alleviate the electron deficiency of the boron atom and, hence, its susceptibility to nucleophilic attack. In compound **1**, however, this is achieved by incorporation of boron into a nonclassical
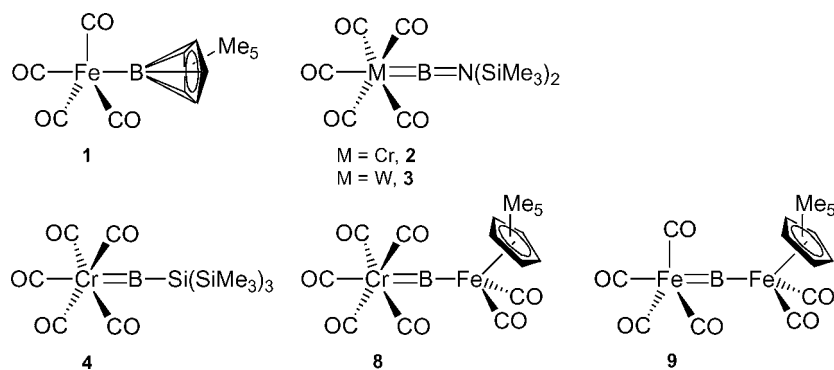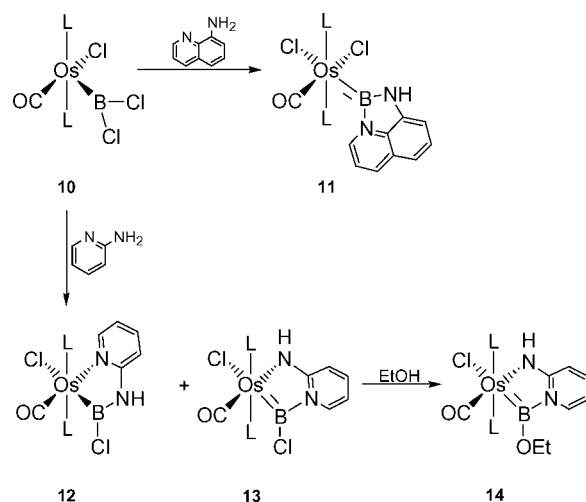
**FIGURE 1** Terminal borylene complexes obtained via salt-elimination reactions.

polyhedral skeleton, making this species a *nido*-pentacarbahexaborane similar to the related main group element derivatives [{(η^5-C$_5$Me$_5$)B}BCl$_3$] and [{(η^5-C$_5$Me$_5$)B}{SiCl$_2$(C$_5$Me$_5$)}][(C$_5$Me$_5$)BCl$_3$] synthesized by Jutzi et al. [29,30] and Siebert et al. [31]. Despite considerable efforts, all attempts at obtaining corresponding complexes [(OC)$_n$M=BNR$_2$] from other aminoboranes X$_2$BNR$_2$ met with no success. However, use of the sterically encumbered silylborane Cl$_2$BSi(SiMe$_3$)$_3$ yielded [(OC)$_5$Cr=BSi(SiMe$_3$)$_3$] (**4**), the first terminal borylene complex featuring a coordinatively and electronically unsaturated boron center (Fig. 1) [23]. The recent realization of the dichloroboryl species [(η^5-C$_5$R$_5$)Fe(CO)$_2$BCl$_2$] (R = H, **5a**; R = Me, **5b**) [32–34], afforded a synthon which could be utilized in the truly remarkable preparation of compounds containing a μ_2-boron bridge. Thus, a double salt-elimination reaction between **5b** and Na$_2$[M(CO)$_n$] (M = Cr, n = 5, **6**; M = Fe, n = 4, **7**) allowed the syntheses and structural characterization of [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}(μ_2-B){Cr(CO)$_5$}] (**8**) and [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}(μ_2-B){Fe(CO)$_4$}] (**9**), the first compounds to contain a boron center classically bonded solely to transition metals (Fig. 1) [34]. In order to circumvent the difficulties and restrictions associated with the synthesis of terminal borylene complexes via salt-elimination reactions, an alternative approach employing boryl species as suitable precursors was successfully pursued by Roper and Aldridge. Accordingly, conversion of the osmium boryl complex [Os(BCl$_2$)Cl(CO)(PPh$_3$)$_2$] (**10**) into the first stable internally base-stabilized terminal borylene species [Os(=BNHC$_9$H$_6$N)Cl$_2$(CO)(PPh$_3$)$_2$] (**11**) upon reaction with 8-aminoquinoline was achieved by Roper et al. (Scheme 1) [22]. Interestingly, the same boryl precursor **10** gave, upon reaction with 2-aminopyridine, a mixture of the tethered-boryl complex **12** and the base-stabilized chloroborylene complex [Os{=BCl(NHC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**13**). Addition of ethanol to this mixture converted **13** into its ethoxyborylene derivative

SCHEME 1 Formation and reactivity of base-stabilized terminal borylene complexes of osmium (L = PPh$_3$).

[Os{=BOEt(NHC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**14**), which could then be separated from the accompanying boryl complex and fully characterized [22]. A corresponding reaction of **10** with 2-(methylamino)pyridine yielded selectively the base-stabilized borylene complex [Os{=BCl(NMeC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**15**) [25].

The first cationic borylene species was reported by Aldridge and coworkers [27]. Addition of Na[BAr$^f_4$] (Ar^f = C$_6$H$_3$(CF$_3$)$_2$-3,5) to a dichloromethane solution of the mesityl(bromo)boryl complex [(η^5-C$_5$Me$_5$)Fe(CO)$_2${B(Br)Mes}] (**16**) (Mes = C$_6$H$_2$(CH$_3$)$_3$-2,4,6) afforded [(η^5-C$_5$Me$_5$)Fe(CO)$_2$=BMes][BAr$^f_4$] (**17**) via bromide abstraction and precipitation of the sparingly soluble NaBr (Eq. (1)).
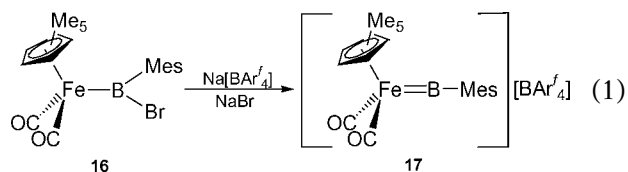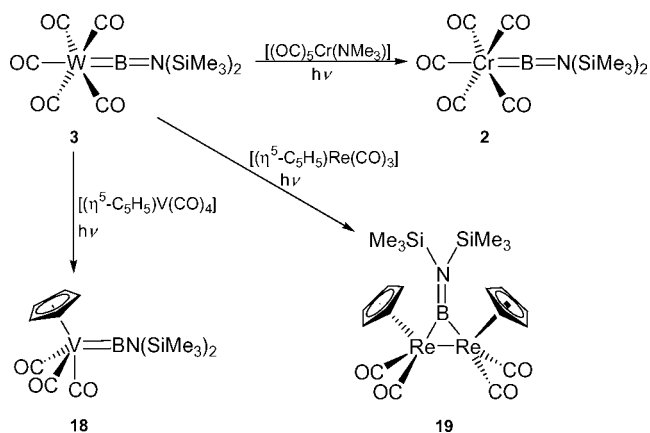
REACTIVITY OF TERMINAL BORYLENE COMPLEXES

As already indicated, the chemistry of terminal borylene complexes is still in its infancy. However, preliminary investigations on the chemistry of the compounds previously described have been conducted, unveiling a rather interesting reactivity. The group VI borylenes $[(OC)_5M=BN(SiMe_3)_2]$ (**2–3**) revealed a remarkable stability toward a range of reagents [35]. Thus, no reaction was observed upon addition of pyridine to a solution of **2** in hexane, while products of borylene displacement were recovered from the reaction of compound **2** with triethylphosphine. Attempts at substituting the amino group at boron with the more reactive chloride ligand upon treatment with hydrogen chloride or boron trichloride led to recovery of the starting materials. Additionally, **2** was not decomposed in the presence of acetone.

In line with Timms' assertion that borylene complexes could represent sources of borylenes in the condensed phase, one of the most remarkable reactions of compounds **2–3** is their ability to transfer the amino borylene unit $BN(SiMe_3)_2$ under photolytic conditions in the presence of suitable borylene acceptors. Hence, upon photolysis of the tungsten compound **3** in the presence of $[(OC)_5Cr(NMe_3)]$, an intermetal borylene transfer to form chromium complex **2** was accomplished (Scheme 2) [24].

While such reaction represented only a proof of concept, constituting an alternative synthesis of an already known species, an analogous procedure, performed in the presence of the vanadium precursor $[(\eta^5\text{-}C_5H_5)V(CO)_4]$ or the rhenium complex $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$, led to the generation of the new terminal and bridged borylene species $[(\eta^5\text{-}C_5H_5)(OC)_3V=BN(SiMe_3)_2]$ (**18**) and $[\{\mu\text{-}BN(SiMe_3)_2\}\{(\eta^5\text{-}C_5H_5)Re(CO)_2\}_2]$ (**19**), respec-

tively (Scheme 2) [24,26]. Most importantly, formation of complexes **18** and **19** emphasizes the synthetic significance of the photochemically induced intermetal borylene transfer, since all attempts at obtaining these products by conventional methods had previously failed.

Unexpected, exciting results came from the reactions of compounds **2–3** with transition-metal-containing Lewis bases. In an attempt to expand the scope of the photochemically promoted borylene transfer as a synthetic route to electronically diverse systems, the reactivity of $[Pd(PCy_3)_2]$ (**20**) as a carbonyl-free borylene acceptor was explored. The electron-rich but highly unsaturated nature of the palladium center in such compounds suggested potentially high reactivity of this species in borylene transfer reactions. Unexpectedly, **20** was shown to be reactive toward the group VI borylenes **2–3** at room temperature *without irradiation*, leading to the formation of the unprecedented heterodinuclear *semibridging* borylene compounds $[(OC)_4M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)]$ (M = Cr, **21**; M = W, **22**) (Eq. (2)) [36].

$$(2)$$
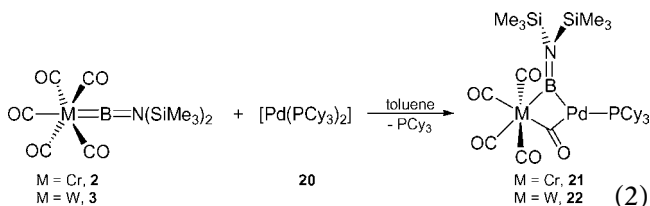
The molecular structure of **21**, as determined by X-ray diffraction, displays an unusual orthogonal orientation of the bis(trimethylsilyl)amino substituent at boron with respect to the plane containing the two transition metals and boron [Si–N–B–Pd: 91.12(15)°]. Such an arrangement differs considerably from that observed in previously reported borylene-bridged species, where the structural parameters imply the presence of a formally sp²-hybridized boron center. In **21** and, by analogy, **22**, however, the disposition of the amino group and the short B–N distance are in line with an sp-hybridization of the boron atom, suggesting that much of the electronic properties of the original terminal borylenes **2–3** are retained in the reaction products **21–22**. Formation of **21–22** was rationalized as stemming from donation of electron density by the Lewis-basic palladium fragment $[Pd(PCy_3)]$ into the π^* orbitals of CO and the empty π-symmetry orbitals of the borylene unit of the electronically saturated borylenes **2,3**. These complexes, therefore, are thought to behave as mere π-acceptor "ligands." Interestingly, the presence of the aforementioned

SCHEME 2 Synthesis of terminal borylene complexes by photochemically promoted borylene transfer.

Pd–B dative interaction makes **21–22** the only examples of transition metal-base-stabilized terminal borylene complexes.

The reactivity that leads to their synthesis suggests that residual Lewis-acidity is unexpectedly retained by the boron atom in **2** and **3** despite the presence of the amino substituent, and testifies for the thermodynamic and kinetic stability of the Cr–B linkage in the complexes. Such behavior differs markedly from that of the cationic iron species $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe=BMes][BAr^f_4]$ (**17**), which, in the presence of neutral nucleophiles, is dominated by borylene displacement (Scheme 3) [37]. Thus, addition of CO to a solution of **17** in dichloromethane resulted in the formation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_3][BAr^f_4]$. Analogously, treatment of **17** with 3,3-dimethyl-1-butene or benzophenone led to isolation of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(CH_2=CH^tBu)][BAr^f_4]$ and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\eta^1\text{-}OCPh_2)][BAr^f_4]$, respectively. The ease of displacement of the B–Mes ligand in the cationic complex **17** contrasts with the high thermodynamic stability of terminal borylene compounds predicted theoretically and at least partially verified experimentally in the case of the group VI borylenes **2,3**. Significant involvement of the dichloromethane solvent in the displacement process, leading to insertion of B—Mes into the C—H bond of the solvent molecules, was inferred by the authors on the basis of kinetic data.

The displacement chemistry is, therefore, thought to be driven by irreversible removal of the B—Mes ligand. A trapping product stemming from insertion of B—Mes into the S—S bond of Me_2S_2 was, indeed, isolated. Borylene displacement or nucleophilic addition to the boron center is the outcome of the reactions between **17** and anionic nucleophiles. Thus, the complete range of asymmetric halide-substituted boryl complexes $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\{B(X)Mes\}]$ [X = F, **23**; X = Cl, **24**; X = Br, **16**; X = I, **25**] are formed upon reaction of **17** with soluble sources of halide anions (Scheme 4),
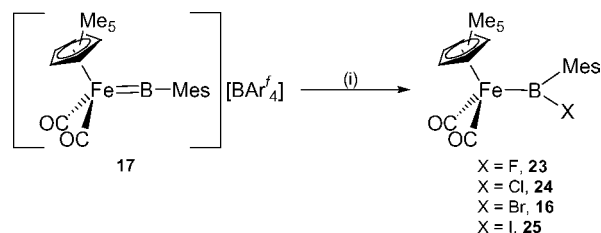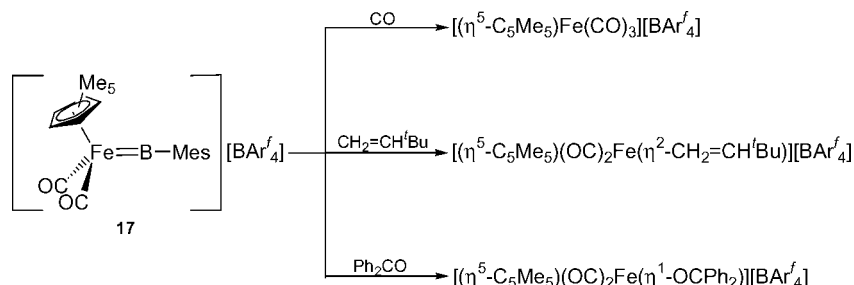

SCHEME 4 Reactivity of the cationic terminal borylene complex **17** toward halide anions (where (i) is halide sources: $[^nBu_4N][BF_4]$, [PPN]Cl, $[Ph_4P]Br$, $[^nBu_4N]I$).

while the phenyl derivative $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2Ph]$ is obtained in the presence of $[PPN][BPh_4]$. Interestingly, the iodo compound $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2I]$ is also formed as a side-product in the reaction that leads to **25**.

Further reactivity of terminal borylene complexes was recently reported by Roper et al. [22,25]. The base-stabilized borylene complex $[Os(=BNHC_9H_6N)Cl_2(CO)(PPh_3)_2]$ (**11**) reacted with ethanol yielding the ethoxy(amino)boryl complex $[Os\{B(OEt)NHC_9H_6N\}Cl(CO)(PPh_3)_2]$ (**26**), following a 1,2-shift of the quinoline-nitrogen atom from boron to osmium (Scheme 5).

The alcoholysis of **11** implies that the boron atom, even in such base-stabilized borylene complex, still displays electrophilic character—a fact already predicted by a theoretical study [1]. The reactivity of the boron and transition metal centers in the base-stabilized borylene complex $[Os\{=BCl(NMeC_5H_4N)\}Cl(CO)(PPh_3)_2]$ (**15**) was also recently investigated, with particular regard to substitution of the chloride ligands. Treatment of complex **15** with $Na[BH_4]$ yielded the osmium hydride species $[Os\{=BCl(NMeC_5H_4N)\}H(CO)(PPh_3)_2]$ (**27**) upon selective substitution of the osmium-bound chloride. Ethanolysis, however, cleaved the B–Cl bond selectively, leading to formation of the ethoxyborylene complex $[Os\{=BOEt(NMeC_5H_4N)\}$

SCHEME 3 Reactivity of cationic complex **17** leading to borylene displacement.
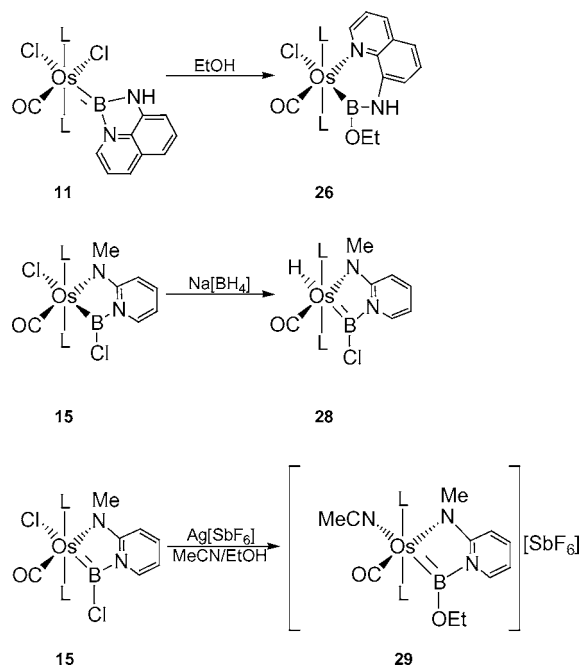
SCHEME 5 Reactivity of the base-stabilized borylene complexes **11** and **15**.

Cl(CO)(PPh$_3$)$_2$] (**28**). Addition of Ag[SbF$_6$] to a solution of complex **15** in a MeCN/EtOH solvent mixture led to abstraction of the osmium-bound chloride and ethanolysis of the B—Cl unit, yielding the cationic borylene complex [Os{=BOEt (NMeC$_5$H$_4$N)}(MeCN)(CO)(PPh$_3$)$_2$][SbF$_6$] (**29**).

SPECTROSCOPIC AND STRUCTURAL ASPECTS

In solution, the most characteristic spectroscopic feature of all terminal borylene complexes featuring two-coordinate boron atoms is a significantly deshielded value of their ^{11}B-NMR resonance with respect to those of corresponding amino- and silylboryl complexes of the type [L$_n$M–B(X)NR$_2$] [15,17] and [L$_n$M–B(X)SiR$_3$] (X = halogen) [38]. The aminoborylene compounds **2**, **3**, and **18** exhibit ^{11}B-NMR signals in the range $\delta = 87$–93 [21,26]. In the absence of heteroatom substitution, a further, considerable downfield shift of the resonance is observed. Thus, the ^{11}B-NMR shift of the cationic iron borylene [(η^5-C$_5$Me$_5$)Fe(CO)$_2$=BMes][BAr$_4^f$] (**17**) is found at $\delta = 158$ [27], that of the silyl-borylene complex [(OC)$_5$Cr=BSi(SiMe$_3$)$_3$] (**4**) at the strikingly deshielded value of $\delta = 204.3$ [23], similarly to those of the two boron-bridged species [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}(μ_2-B){Cr(CO)$_5$}] (**8**) and [{(η^5-C$_5$Me$_5$)Fe(CO)$_2$}(μ_2-B){Fe(CO)$_4$}] (**9**) at

$\delta = 204.6$ and 190.9, respectively [34]. Due to the higher coordination numbers of their boron centers, [(OC)$_4$Fe—B(η^5-C$_5$Me$_5$)] (**1**) [28] and [Os{=BOEt(NHC$_5$H$_4$N)}Cl(CO)(PPh$_3$)$_2$] (**14**) [25] display much more shielded ^{11}B-NMR resonances at $\delta = -35.3$ and 52.1, respectively, the former being characteristic for apical boron atoms in such *nido*–carboranes.

Crystallographic data were collected for most of the compounds discussed above and utilized, with the aid of theoretical calculations, to rationalize the bonding situation in terminal borylene species. The metal–boron distances in the aminoborylene complexes **2**,**3**, and **18** range from 1.959(6) to 2.151(7) Å. The Cr—B bond length in the boron-bridged complex **8** [1.975(2) Å] is moderately shorter than that in the aminoborylene **2** [1.996(6) Å], while a considerable shortening of the corresponding distance is observed in the silylborylene **4** [1.878(10) Å]. This is line with an increased Cr–B π-back-donation in **4** than in **2** as a consequence of the pronounced electron-deficiency of the boron atom in the former compound. The cationic complex [(η^5-C$_5$Me$_5$)Fe(CO)$_2$=BMes][BAr$_4^f$] (**17**) shows an orientation of the mesitylborylene ligand in the crystal that allows for π-donation from the metal center and the mesityl ring into the two vacant perpendicular p orbitals at boron. The Fe—B distance of 1.792(8) Å is, thus, shorter than any reported transition metal–boron linkage, including those in the boron-bridged species **9** [1.863(2) and 1.867(2) Å] and is consistent with a Fe—B double bond. In contrast, for the complex [(OC)$_4$Fe—B(η^5-C$_5$Me$_5$)] (**1**), which exhibits a six-coordinate borylene ligand in axial position, a significantly longer iron–boron distance of 2.010 Å was reported, indicating the single bond character of such linkage. The base-stabilized borylene complex **23** is characterized by an Os—B distance of 2.066(5) Å, thus longer than that expected for a double bond and consistent with the higher coordination number of boron in such compound.

CONCLUSIONS

Since the report on the first structurally authentic terminal borylene compound [(OC)$_5$W=BN(SiMe$_3$)$_2$] in 1998, the chemistry of these materials has developed into a topical area of research. A number of synthetic methods provide access to a variety of coordination environments for the borylene ligand. Although all the protocols present significant limitations with respect to the types of suitable precursors, photochemically promoted borylene transfer and salt-elimination reactions have proven to be the most general synthetic routes, the latter

providing access to the remarkable boron-bridged species $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}(\mu_2\text{-}B)\{Cr(CO)_5\}]$ and $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}(\mu_2\text{-}B)\{Fe(CO)_4\}]$. Initial studies on the reactivity of such complexes suggest that general patterns might be difficult to assign. Indeed, the B—M linkage in group VI aminoborylene complexes $[(OC)_5M\text{=}BN(SiMe_3)_2]$ proved to be stable in a variety of conditions, yet reactive toward the transition-metal Lewis base $[Pd(PCy_3)_2]$ to form the unprecedented semibridging borylenes $[(OC)_4M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)]$. The analogous unit in $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe\text{=}BMes][BAr_4^f]$, however, appeared more labile and prone to displacement. More studies are awaited to further clarify the properties of these compounds and hence envisage their future applications.

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