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C–H Activation

Carbene–Transition Metal Complexes Formed by Double C–H Bond Activation

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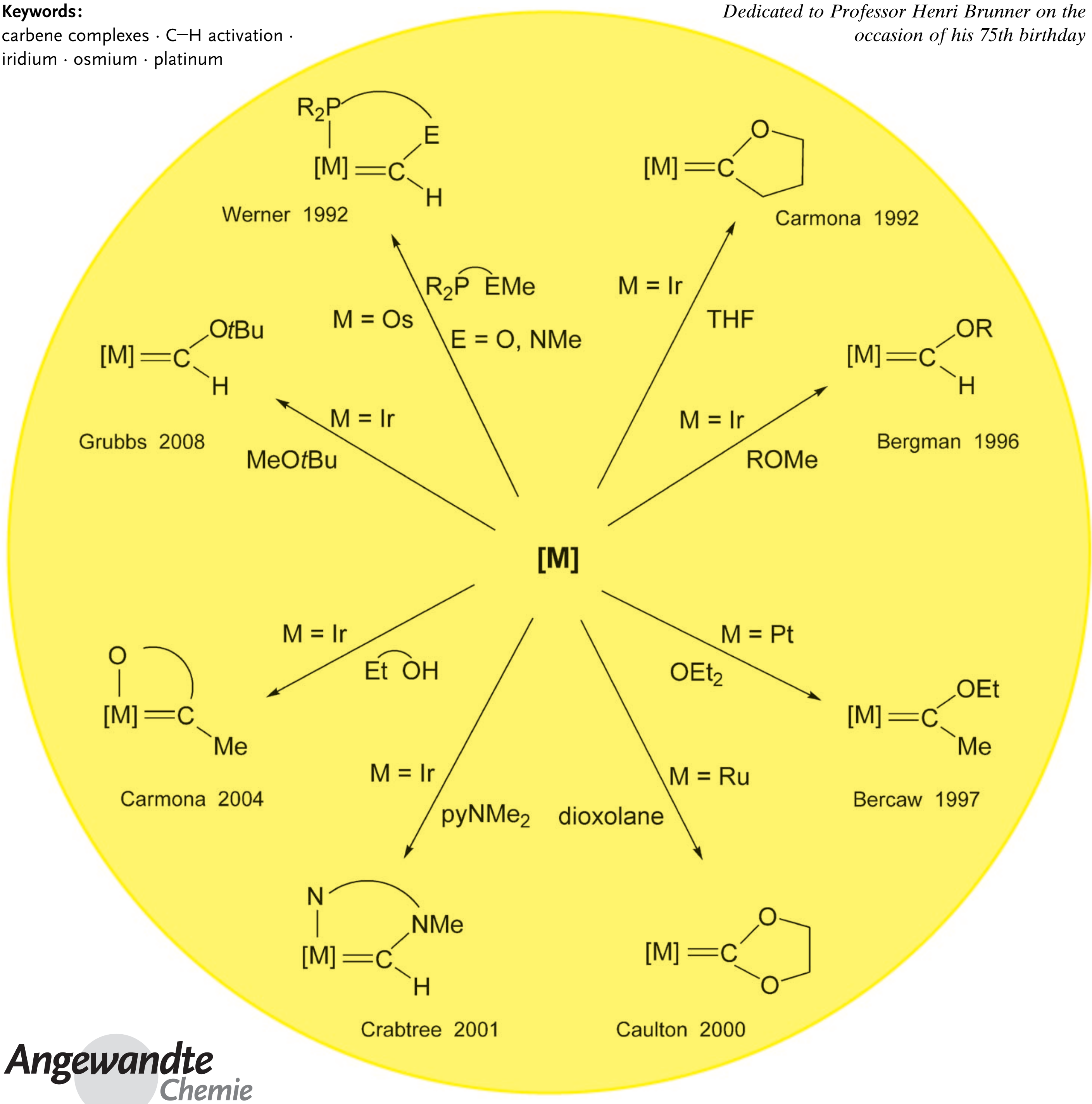
carbene complexes · C–H activation · iridium · osmium · platinum

Dedicated to Professor Henri Brunner on the occasion of his 75th birthday



The activation of a single sp^3 C–H bond of alkanes and their derivatives by electron-rich transition metal complexes has been a topic of interest since the landmark work by Bergman and Graham in 1982. Ten years later, it was shown that compounds of 5d elements, such as osmium and iridium, even enable a double α-C–H bond activation of alkane or cycloalkane derivatives containing an OR or NR$_2$ functional group, thus opening up a new route to obtain Fischer-type transition metal carbene complexes. Subsequent work focused in particular on the conversion of methyl alkyl and methyl aryl ethers into bound oxocarbenes and also of dimethyl amines to bound aminocarbenes. In the context of this work, it was recently shown that square-planar oxocarbene–iridium(I) complexes prepared in this way exhibit an unusual mode of reactivity: They react with CO$_2$, CS$_2$, COS, PhNCO, and PhNCS by an atom- or group-transfer metathesis, which has no precedent. Organic azides RN$_3$ and N$_2$O behave similarly. Recent results confirm that this novel type of metathesis can be made catalytic, thus offering a novel possibility for C–H bond functionalization.

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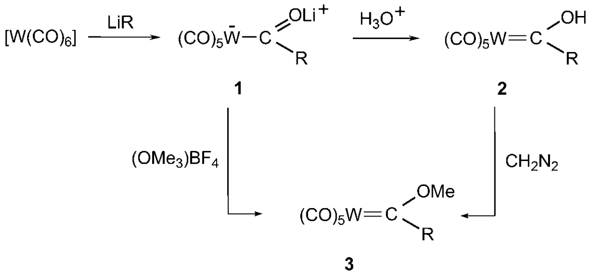
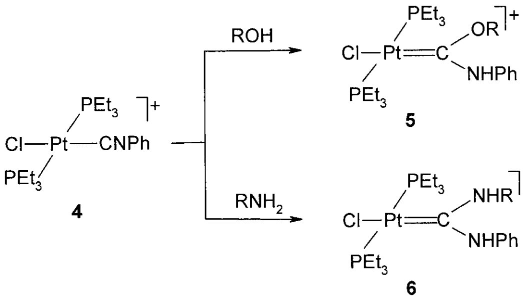
1. Introduction

The preparation and structural characterization of the methoxy(phenyl)carbene–tungsten complex [W{C(OMe)Ph}(CO)$_5$] (**3**) by Fischer and Maasböl in 1964 represented a landmark in organometallic chemistry.[1] In the first step, the synthetic procedure involved the generation of the tungsten acylate **1** by attack of phenyllithium on one of the CO ligands of [W(CO)$_6$]. After protonation of the acylate to the hydroxycarbene **2** and reaction of this labile intermediate with diazomethane, the tungsten carbene **3** was formed (Scheme 1). Shortly thereafter, it was shown that this procedure could be shortened by directly converting the acylate **1** with Meerwein's oxonium salt (Me$_3$O)BF$_4$ into complex **3**.[2] Using this methodology, CO ligands of chromium, molybdenum, manganese, technetium, rhenium, iron, and nickel carbonyl complexes could be readily transformed into coordinated carbenes.[3]



Scheme 1. R = Ph.

The Fischer and Maasböl work, together with the subsequent publications from Fischer's laboratory, meant not only the discovery of a new research field, but it also awakened the interest of several research groups to find other routes than those used by Fischer to prepare transition metal carbene complexes. In 1969, Chatt reported that cationic metal isocyanides, such as [PtCl(CNPh)(PEt$_3$)$_2$]$^+$ (**4**), reacted with primary alcohols or primary amines to the amino(alkoxy)carbene and bis(amino)carbene complexes **5** and **6** by addition of the alcohol O–H or the amine N–H bond to the C–N multiple bond of the isocyanide (Scheme 2).[4] Even complexes of the general composition [M{C(NHMe)$_2$}$_4$]$^{2+}$ (M = Pd, Pt), which were the first to contain only carbene ligands, were obtained by this route.[5] More recent work by Hahn showed that the nucleophilic attack of an NH$_2$ functionality at an isocyanide carbon atom can also be carried out in an intramolecular fashion, leading to five-membered heterocyclic bis(amino)carbene ligands.[6]



Scheme 2.

A more general method to generate bis(amino)carbene ligands at a transition metal center was developed by Lappert, who used tetrakis(amino) olefins, such as **7**, as carbene sources. Upon treatment with the chloro-bridged platinum(II) compound **8**, cleavage of the C–C bond occurred, and half of the electron-rich olefin coordinated, yielding the mononuclear complex **9** (Scheme 3).[7] It is interesting to note

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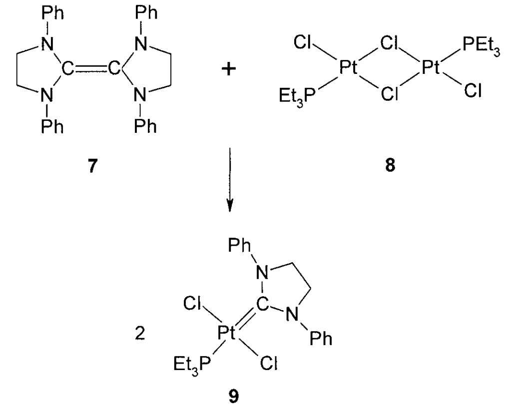
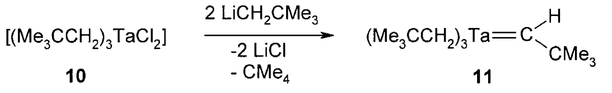


Scheme 3.

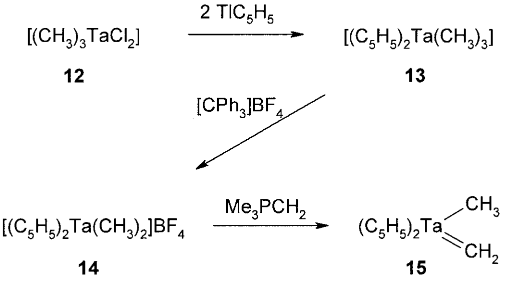
that about 25 years later, the type of ligand found in **9** was among the first to be isolated in pure (that is, uncoordinated) form and belongs to the group of carbenes which are now generally described as Arduengo carbenes.[8] With $[Me_2N{=}CHCl]Cl$ (Vilsmeyer's reagent) as precursor, Lappert also succeeded in preparing a series of complexes of the general composition $[M\{CH(NMe_2)\}L_n]$, which were the first to have secondary carbenes as ligands.[9]

A further big step in the development of carbene–metal chemistry was achieved in 1974 by Schrock. With the aim of preparing pentakis(neopentyl)tantalum, $[Ta(CH_2CMe_3)_5]$, from **10** and two equivalents of $LiCH_2CMe_3$, he obtained the surprisingly stable carbene complex **11** (Scheme 4).[10,11] It



Scheme 4.

is probably formed via $Ta(CH_2CMe_3)_5$ as intermediate, which reacts by α-H abstraction and elimination of CMe_4 to give the product.[12] In continuing the work on the reactivity of alkyl tantalum compounds, Schrock also isolated the first methylene transition metal complex **15**, using **12** as the starting material (Scheme 5).[13] Prior to Schrock's work, attempts to prepare mononuclear transition metal compounds with the $M{=}CH_2$ core were carried out by Pettit, Green, Herrmann, and others, but they could at best trap the coordinated CH_2 species with an olefin from the short-lived $[M(CH_2)L_n]$ intermediate or stabilize the intermediate by transforming it into a dinuclear derivative with a $M(CH_2)M$ bridge.[14]

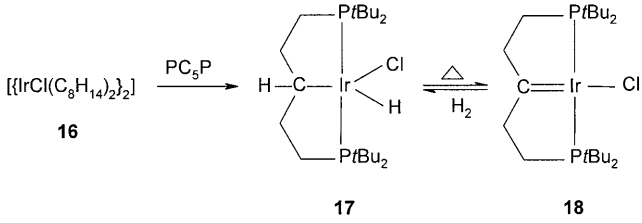


Scheme 5.

Helmut Werner studied chemistry in Jena and Munich and received his PhD with E. O. Fischer in 1961. After postdoctoral work with J. H. Richards at Caltech, he became Professor of Inorganic Chemistry at the University of Zurich and was appointed Professor and Head of the Institute of Inorganic Chemistry at the University of Würzburg in 1975. Since 2002, he is Emeritus Professor. Apart from numerous international awards, he received the prestigious Alfred Stock Prize of the German Chemical Society in 1988 and was elected as a member of the Academy Leopoldina (now: National Academy of Sciences) in the same year. He received honorary doctorates from the University of Zaragoza (2001) and from the University of Jena (2006).

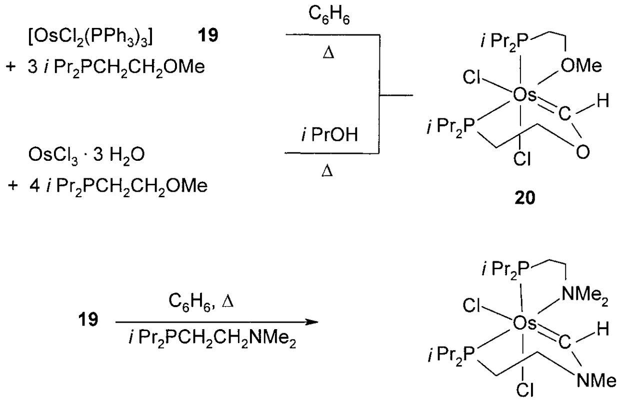
2. First Results

The first hint that an electron-rich transition metal is able to generate a coordinated carbene by double C–H bond activation was reported by Shaw and co-workers in 1977. They found that the reaction of the chelating ligand 1,5-$C_5H_{10}(PtBu_2)_2$ (Scheme 6) with the cyclooctene–iridium(I) dimer **16** results in a C–H oxidative addition to give the pincer-type iridium(III) derivative **17**, which upon sublimation releases H_2 and affords the stable four-coordinate iridium(I) complex **18**. In the presence of hydrogen, the alkyl(hydrido) compound **17** is reformed.[15] The X-ray crystal structure analysis of **18** confirmed the square-planar coordination around iridium and revealed an Ir–C bond of 2.006(4) Å as the most important feature; the length of this bond lies somewhere between the values expected for an iridium(I) carbene and an iridium(III) ylide. This is in agreement with the ^{13}C NMR data, which also favor a substantial contribution from the ylide form.[15]



Scheme 6. $PC_5P = 1,5\text{-}C_5H_{10}(PtBu_2)_2$.

Fifteen years passed before the next two examples of double C–H bond activation were disclosed. As part of our work on the chemistry of coordinatively unsaturated osmium compounds with a 14- or 16-electron count,[16] we attempted to prepare complexes of the general composition $[OsX_2(PR_3)_2]$ (X = halide) as analogues of the well-known phosphine iron(II) derivatives $[FeX_2(PR_3)_2]$.[17] After initial attempts failed, we focused our interest on the synthesis and reactivity of corresponding osmium chelates $[OsX_2(L\text{-}L')_2]$ with phosphinoethers $i\mathrm{Pr_2PCH_2CH_2OR}$ and phosphinoesters $i\mathrm{Pr_2PCH_2CO_2R}$ (R = Me, Et) as bidentate, though hemilabile, ligands. This seemingly simple approach of obtaining, for example, $[OsCl_2(i\mathrm{Pr_2PCH_2CH_2OMe})_2]$ from $[OsCl_2(PPh_3)_3]$ (**19**) and $i\mathrm{Pr_2PCH_2CH_2OMe}$, which in the case of the analogous reaction of $[RuCl_2(PPh_3)_3]$ and $i\mathrm{Pr_2PCH_2CH_2OMe}$ gave $[RuCl_2(i\mathrm{Pr_2PCH_2CH_2OMe})_2]$ exclusively,[18] led surprisingly to the Fischer-type oxocarbene osmium(II) complex **20** (Scheme 7). A more favorable procedure for the preparation of **20** is the reaction of $OsCl_3{\cdot}3H_2O$ with $i\mathrm{Pr_2PCH_2CH_2OMe}$ in boiling isopropanol, affording the carbene complex in excellent yield.[19a]



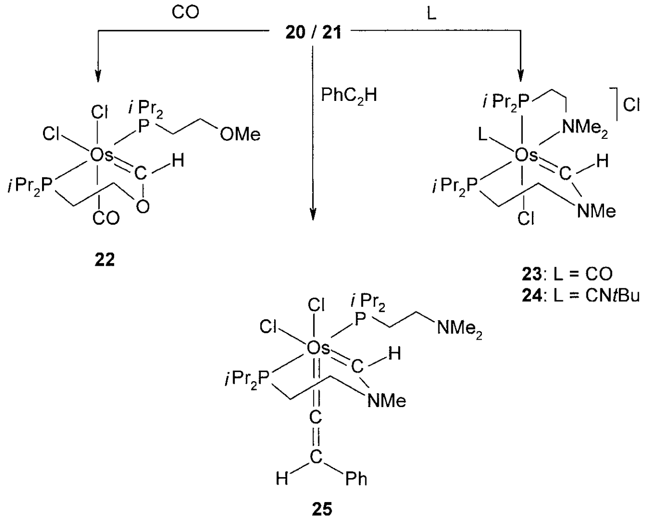
20

21

Scheme 7.

The X-ray crystal structure analysis of **20** confirmed the generation of the carbene unit by double metalation of a methoxy group. It also revealed that the carbene carbon atom is part of a six-membered chelate ring and is *trans* to a chloro ligand. The two phosphorus atoms are in *cis* positions and *trans* to the second chloro ligand and the methoxy moiety of the coordinated phosphinoether. Taking into consideration that complex **20** is chiral, it is quite remarkable that in the single crystal used for the structure determination, only one enantiomer is present.[19a]

The reaction of $OsCl_3{\cdot}3H_2O$ with $i\mathrm{Pr_2PCH_2CH_2NMe_2}$ under the same conditions as used for the preparation of **20** led to a mixture of products that contained only about 40–50% of the aminocarbene complex **21**. However, with **19** as starting material and benzene as solvent, **20** was formed as the main product and isolated in good yield.[19a,b] By comparing the ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy data of **21** with those of **20**, there was no doubt that the structures of the two compounds were similar. The reactivity of **20** and **21** is also related in that upon treatment with CO and CN*t*Bu, the Os=C bond is maintained and the six-membered chelate ring containing the carbene fragment is unchanged (Scheme 8). Moreover, a crystallographic study of **23** revealed that the structure of the cation is similar to that of **20**, the only difference being that the carbene carbon atom is *trans* to CO and not to the chloro ligand.[19b] The $Os{-}C_{carbene}$ bond in **23** is significantly elongated compared to the uncharged complex **20**, thus reflecting the *trans* influence of CO on one hand and the positive charge of the cation on the other. The reaction of **21** with phenylacetylene led to the vinylidene derivative **25**, which is possibly formed by the isomeric alkyne and alkynyl(hydrido) species as intermediates. Compound **25** is a rare example of a complex with both a carbene and a vinylidene ligand bound to a single transition metal center.[3,20]



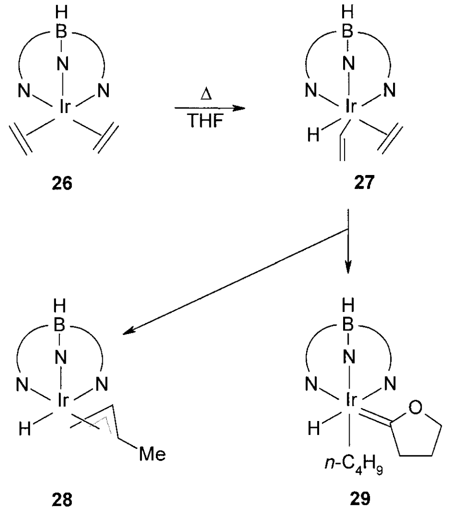
22

23: L = CO
24: L = CN*t*Bu

25

Scheme 8.

In work that was simultaneous but independent of our results on osmium carbenes, Carmona and co-workers discovered a novel route to Fischer-type iridium carbenes by double α-C–H bond activation. In the course of studies aimed at C–H bond cleavage followed by C–C bond formation induced by tris(pyrazolyl) hydroborato iridium compounds, Carmona et al. found that heating a solution of the bis(ethene) iridium(I) derivative **26** in tetrahydrofuran afforded a circa 1:1 mixture of the allyl hydrido and the *n*-butyl hydrido oxocarbene iridium(III) complexes **28** and **29** in nearly quantitative yield (Scheme 9).[21] The two products



26 **27** **28** **29**

Scheme 9. The anionic tridentate ligand HBN_3 is tris(3,5-dimethylpyrazol-1-yl)hydroborate.

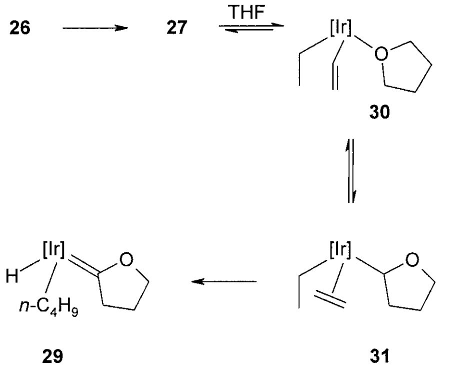
originate from **26** by two competitive pathways via the isolable intermediate **27**.[22] This species converts quantitatively into the isomer **28** when cyclohexane is used as the solvent instead of THF. NMR spectroscopy studies confirmed that **28** is not a precursor for the carbene derivative **29**. Other five- and six-membered cyclic ethers undergo analogous double C–H bond activation, provided a CH_2O functionality exists.[21,23,24] Five-membered heterocycles were more reactive than related six-membered counterparts, and two heteroatoms (in particular oxygen) in the ring favored the formation of the ligated carbenes. Despite the different coordination sphere and oxidation state, the $M{-}C_{carbene}$ bond in **29** is similar in length to that in **20**.[21]

Subsequent to Carmona's investigations, Li and Taube reported the preparation of an octahedral osmium(II) complex of the composition $[Os(NH_3)_4(\eta^2\text{-}H_2)\{{=}CO(CH_2)_3\}]^{2+}$, which contained the same cyclic oxocarbene ligand as found in **29.** The cation was formed by the reduction of $[Os(NH_3)_4(CF_3SO_3)_2]CF_3SO_3$ with Zn/Hg in THF at room temperature, and was unequivocally characterized by analytical and spectroscopic means. In contrast to Carmona's results, the reaction of $[Os(NH_3)_4(CF_3SO_3)_2]CF_3SO_3$ with Zn/Hg in tetrahydropyran also led to an oxocarbene complex containing a six-membered $CO(CH_2)_5$ ring. Similar experiments with tetrahydrothiophene failed, presumably because of the stability of the precursor osmium(II) species with the coordinated thioether.[25]

3. Mechanistic Considerations

The landmark papers by Fischer and Schrock not only attracted world-wide attention but also raised the question as to whether the most simple carbene, methylene CH_2, could be generated from CH_4 in the coordination sphere of a transition metal. After early attempts undertaken in the 1960s failed,[26] the formation of M–C bonds by C–H bond activation of methane and other alkanes was made feasible by the work of Bergman and Graham about two decades later. Both groups simultaneously but independently observed that iridium(I) and iridium(III) compounds, such as $[(C_5Me_5)Ir(CO)_2]$ and $[(C_5Me_5)IrH_2(PMe_3)]$, afforded short-lived, 16-electron intermediates $[(C_5Me_5)Ir(L)]$ (L = CO, PMe_3) under UV irradiation; in the presence of alkanes or cycloalkanes, these species gave iridium(III) complexes of the general composition $[(C_5Me_5)IrH(R)(L)]$ (R = CH_3, CH_2CMe_3, $c\text{-}C_6H_{11}$, etc.) by single α-C–H bond activation.[27,28] The crucial point in preparing these alkyl(hydrido) and cycloalkyl(hydrido) derivatives (and of the analogous cyclopentadienyl compounds $[(C_5H_5)IrH(R)(L)]$ as well)[28b] was the use of inert solvents, such as perfluoroalkanes or noble gases, that do not react with the labile 16-electron intermediate $[(C_5Me_5)Ir(L)]$ by oxidative addition. Bergman's and Graham's work was supplemented by that of Jones and Feher, which confirmed that $[(C_5Me_5)RhH_2(PMe_3)]$ behaved similarly to the iridium counterpart and reacted with alkanes and cycloalkanes photochemically to give rhodium(III) complexes $[(C_5Me_5)RhH(R)(PMe_3)]$.[29] The sensitive alkyl- and cycloalkyl hydrido compounds $[(C_5Me_5)MH(R)(L)]$ (M = Rh, Ir) could be converted into the more stable alkyl- and cycloalkyl(halogeno) derivatives $[(C_5Me_5)MX(R)(L)]$ (X = Cl, Br), which were fully characterized by spectroscopic and, in some cases, crystallographic techniques. Though it was well-known at the time that α-H abstraction could be preferred over β-H abstraction from a $[M(CH_2CH_2R)(L)_n]$ precursor,[30] attempts to transform compounds of the composition $[(C_5Me_5)MH(R)(L)]$ or $[(C_5Me_5)MX(R)(L)]$ into products with a methylene or carbene ligand by elimination of H_2 or HX remained unsuccessful.

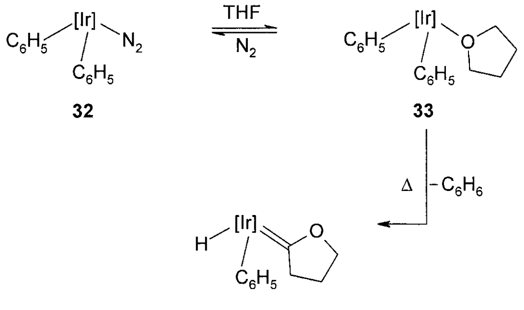
The reason that complexes such as **20**, **21**, and **29** (Scheme 7 and 9) could be obtained by double α-C–H bond activation from precursors with a OCH_3, NCH_3, or OCH_2R moiety must therefore be due to the presence of the heteroatom. With regard to the preparation of **20** and **21**, we proposed that the first step of each reaction is the coordination of the P*i*Pr₂ group of the functionalized phosphine at the osmium atom, followed by the formation of the chelate ring by Os–O or Os–N bonds. The insertion of the metal into one of the C–H bonds of the OCH_3 or NCH_3 units then occurs intramolecularly, leading to intermediates with an alkyl hydrido osmium fragment $ROCH_2OsH$ or $RN(CH_3)CH_2OsH$. The α-H abstraction from the metal-bound methylene unit in the last step is probably favored by the restricted rotation around the carbon atom of the $OsCH_2X$ unit, which brings the C–H bond to be cleaved in close proximity to the metal and finally promotes the elimination of the H_2 molecule.[19]



Scheme 10. [Ir] is the tris(3,5-dimethylpyrazol-1-yl)hydroborate iridium(III) fragment.

Carmona proposed a somewhat different mechanism to explain the formation of the iridium oxocarbene **29** from **26** as precursor (Scheme 10).[21,23] The initial step in this case is undoubtedly the intramolecular oxidative addition of a C–H ethene bond to the metal, yielding the hydrido(vinyl) complex **27** which, as mentioned above (see Scheme 9), has been isolated and completely characterized.[22] It was supposed that the subsequent coordination of the cyclic ether was accompanied by the insertion of the ethene ligand into the Ir–H bond, leading to the THF adduct **30**. The next step should consist of the cleavage of the first of the α-hydrogen atoms of THF, which couples to the σ-bonded vinyl carbon to generate the ethene(ethyl) metal intermediate **31**. The formation of this intermediate has been confirmed by labeling studies with $[D_8]$THF. Lastly, **31** transforms via α-H elimination and insertion of ethene into the Ir–C_2H_5 linkage to give the product **29**. Deuteration studies indicate that both the coordination of THF and the first C–H activation step are reversible. Carmona draw particular attention to the fact that, despite the existence of β-hydrogen atoms in the ethyl unit, the intermediate **31** does not convert into an isomeric 1-butene hydrido species, probably because of the higher thermodynamic stability of the Fischer-type oxocarbene complex **29**.[23] The entire mechanism (Scheme 10), including the coordination of THF followed by two consecutive α-H elimination steps, is in good agreement with Li and Taube's results.[25]

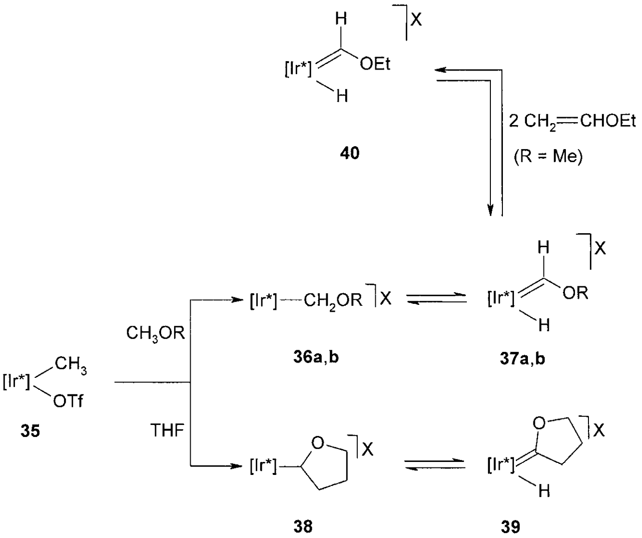
Additional work by Carmona's group also supported the mechanism explaining the formation of **29**. It was found that various tris(pyrazolyl)hydroborato iridium complexes that are able to generate a [Tp′Ir(R)(R′)] fragment (Tp′ = tris(3,5-dimethylpyrazol-1-yl)hydroborate; R,R′ = H, alkyl, aryl) and that have a vacant or readily available coordination site react with THF by double α-C–H bond activation.[23] A typical example is the reaction of the ethene(hydrido) iridium(III) compounds $[Tp'IrH(R)(C_2H_4)]$ (R = H, Et) with THF at 60 °C, which leads cleanly to the carbene complexes $[Tp'IrH(R)\{{=}CO(CH_2)_3\}]$. Owing to the lability of the olefinic ligand, there is no insertion of ethene into the Ir–H or Ir–C bond, and the C–H activation thus becomes the only accessible route. The bis(phenyl) derivative **32** (Scheme 11) undergoes an analogous reaction to afford the hydrido oxocarbene complex **34**. NMR experiments using $[D_8]$THF as the solvent supported the generation of $[D_8]$-**33** as intermediate. This species reconverts smoothly into the starting material **32** upon heating in an N_2 atmosphere.[23]



Scheme 11. [Ir] is the tris(3,5-dimethylpyrazol-1-yl)hydroborate iridium(III) fragment.

4. Noncyclic Ethers and Tertiary Amines as Substrates

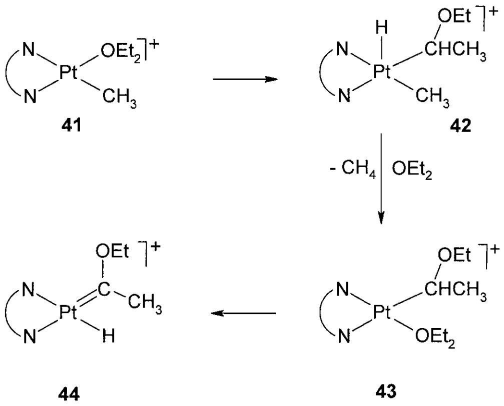
The first example of double C–H bond activation with non-cyclic ethers was reported in 1996.[31] Following the seminal work on the oxidative addition of methane and other alkanes to reactive iridium(I) species, such as $[(C_5Me_5)Ir(PMe_3)]$, Bergman et al. reported that the iridium(III) triflate $[(C_5Me_5)(PMe_3)Ir(CH_3)(OTf)]$ (**35**, $OTf = OSO_2CF_3$), which had already been shown to be capable of activating non-functionalized sp^2 and sp^3 C–H bonds of hydrocarbons,[32] reacted with methyl ethers CH_3OR ($R = CH_3$, $t\text{-}C_4H_9$) at room temperature to give the cationic oxocarbene hydrido complexes **37a,b** (Scheme 12). The reaction could be extended to the formation of **39**, generating the same cyclic carbene ligand as found in Carmona's derivative **29** (Scheme 9). The formation of **37a,b** and **39** proceeds by initial σ-bond metathesis to furnish the intermediate alkoxomethyl species **36a,b** and **38**, which subsequently rearrange to the stable carbene complexes by a rapid α-hydrogen migration. The lability of the triflate ligand presumably facilitates the displacement of the CH_3 group by the CH_2OR unit. The alkoxomethyl intermediate **36a**, which is in equilibrium with the metal carbene **37a**, could be trapped by addition of Lewis bases L, such as CO, CN*t*Bu, and C_2H_4, yielding the cationic complexes $[(C_5Me_5)(PMe_3)Ir(CH_2OR)(L)]X$. Thermolysis of **37a** in THF at 105 °C resulted in the formation of **39** and dimethyl ether, which is consistent with the reversible generation of the unsaturated intermediate **36a**.[31]



Scheme 12. [Ir*] is $[(C_5Me_5)(PMe_3)Ir]$; **36a,37a**: R = Me; **36b,37b**: R = *t*Bu; X = OTf or BPh_4 or $B[C_6H_3(CF_3)_2]_4$ after anion exchange.

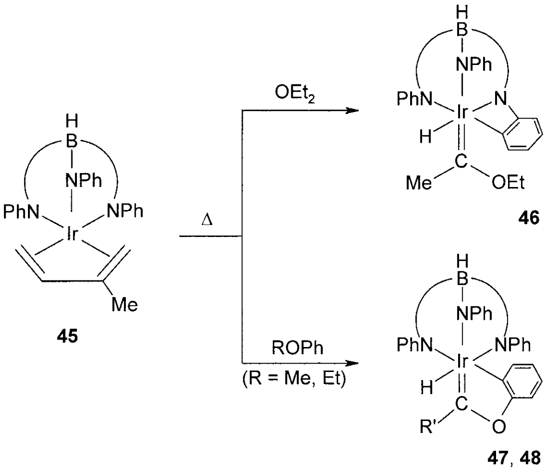
The cationic oxocarbene hydrido complex **37a** undergoes another subsequent reaction, for which there was no precedent. Addition of two equivalents of ethyl vinyl ether to a solution of **37a** gave the ethoxy-substituted counterpart **40** and $MeOCH{=}CH_2$ (Scheme 12).[31] The exchange process does not involve cleavage of the carbon–carbon double bond of ethyl vinyl ether, as treatment of **40** with 2-methoxypropene resulted in the exclusive formation of **37a** and not the Fischer-type carbene derivative $[(C_5Me_5)(PMe_3)IrH\{C(OMe)Me\}]BPh_4$. This product would have been expected if the reaction mechanism was similar to that involved in olefin metathesis. Further experiments with ^{17}O-enriched **37a** indicated that the exchange involves the formal transfer of alkoxy groups between the alkoxycarbene complex and the vinyl ether. Bergman assumed that the initial step consists in the coordination of the ether ROCH=CH$_2$ via the C=C bond to the 16-electron species **36a**, which is followed by an intramolecular attack by the pendant methoxy group of the CH$_2$OMe ligand at the olefin. The resulting labile intermediate containing a cyclic five-membered IrCH$_2$CH(OR)O(Me)CH$_2$ unit can then return along an analogous pathway to complete the exchange.[31] This mechanism is supported by previous work of Thorn and Tulip on the reactivity of alkoxymethyl iridium complexes with electrophilic carbon centers.[33]

Shortly after Bergman's paper appeared, Holtcamp, Labinger, and Bercaw reported that a double α-C–H bond activation of diethyl ether can be accomplished at a cationic platinum(II) center.[34,35] The addition of an equimolar amount of Brookhart's acid [H(OEt$_2$)$_n$][B(Ar$_F$)$_4$] (Ar$_F$ = 3,5-C$_6$H$_3$(CF$_3$)$_2$) to a solution of [(tmeda)Pt(CH$_3$)$_2$] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) in Et$_2$O at −70 °C afforded the substitution product **41** (Scheme 13). This compound is stable at low temperature, but it reacts in solution at room temperature to yield the oxocarbene hydrido complex **44** and methane. The primary step of the reaction probably consists in the oxidative addition of an α-C–H bond of the coordinated ether at the metal to give the alkyl(hydrido)platinum(IV) intermediate **42**, which after elimination of CH$_4$ and coordination/de-coordination of Et$_2$O ultimately gives the stable carbene complex **44** via intermediate **43**. Addition of one equivalent of [H(OEt$_2$)$_n$][B(Ar$_F$)$_4$] to a solution of [(tmeda)Pt(CH$_3$)$_2$] in THF affords the labile cation [(tmeda)Pt(CH$_3$)(thf)]$^+$, which reacts at room temperature by elimination of methane to the cation [(tmeda)PtH{=CO(CH$_2$)$_3$}]$^+$ that contains the cyclic oxocarbene ligand found in **29**, **34**, and **39**.[36] That methylplatinum(II) complexes can undergoe not only an intra- but also an intermolecular sp^3 C–H activation was demonstrated by the reactions of [(tmeda)Pt(CH$_3$)(NC$_5$F$_5$)][B(Ar$_F$)$_4$] (NC$_5$F$_5$ = pentafluoropyridine) with ^{13}CH$_4$ and C$_6$H$_6$, which led to the formation of the cations [(tmeda)Pt(^{13}CH$_3$)(NC$_5$F$_5$)]$^+$ (NC$_5$F$_5$ = pentafluoropyridine) and [(tmeda)Pt(C$_6$H$_5$)(NC$_5$F$_5$)]$^+$, respectively.[34,36]



Scheme 13. The chelate ligand is tetramethylethylenediamine.

Using a more bulky analogue of the tris(pyrazolyl)hydroborato ligand Tp′ (Scheme 10 and 11) with a phenyl group as a substituent at the 3-position of the pyrazolyl rings, Carmona et al. also succeeded in the preparation of an oxocarbene–iridium complex by double α-C–H bond activation of diethyl ether.[37] Heating a solution of the isoprene–iridium(I) precursor **45** in Et$_2$O at 60 °C gave the ethoxy(methyl)carbene–hydridoiridium(III) compound **46** in excellent yield (Scheme 14). This complex is probably formed by a multistep reaction pathway that includes the cleavage of two α-C–H bonds of diethyl ether and the cyclometalation of the phenyl substituent of one of the pyrazolyl rings. The isoprene ligand acts as an intramolecular dihydrogen scavenger and is transformed into the leaving group 2-methyl-2-butene. The thermal reactions of **45** with anisole and ethoxybenzene also give rise to double α-C–H bond activation, though in these cases the phenyl ring of the ether substrate undergoes cyclometalation. The preferred formation of **47** and **48** indicates that the putative less-strained metalation of the six-membered ring attached to the carbene oxygen atom prevails over that of the pyrazolyl unit.

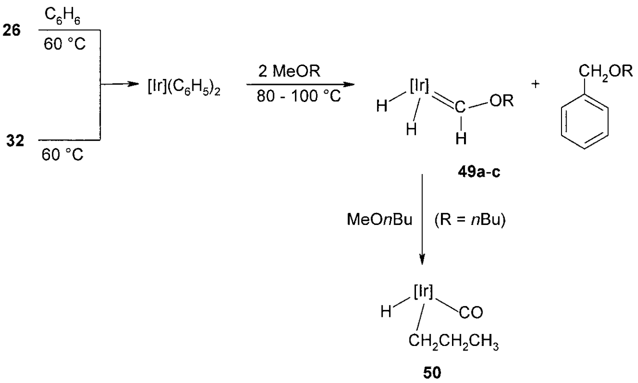


Scheme 14. The anionic tridentate ligand HB(NPh)$_3$ in **45** and **47**, **48**, drawn in simplified fashion, is tris(3-phenylpyrazol-1-yl)hydroborate; **47**: R′ = H, **48**: R′ = Me.

The isoprene derivative **45** not only reacts with non-cyclic ethers, but also with THF to afford an oxocarbene complex that is structurally related to **46** and has the same five-membered {Ir=CO(CH$_2$)$_3$} unit found in **29**.[37] Labeling experiments with [D$_8$]THF confirmed that one of the THF hydrogen atoms generated the Ir–H unit. The analogue of **45**, with 2,3-dimethylbutadiene as bidentate ligand instead of isoprene, reacts even faster with THF, furnishing the same product as generated from **45**.[38] A precursor with 2-thienyl instead of phenyl substituents at the three pyrazolyl rings and 2,3-dimethylbutadiene as olefinic ligand is much less reactive, and in refluxing THF gives an analogue of **46** that has a cyclometallated thienyl group.[38]

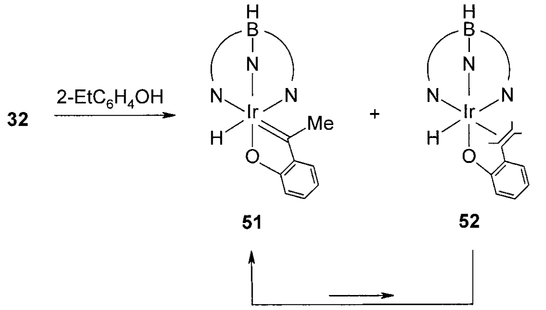
Apart from **45**, the coordinatively unsaturated fragment {(Tp′)Ir(C$_6$H$_5$)$_2$}, readily generated from **32** or from **26** and benzene, is also able to activate two α-C–H bonds of anisole

($CH_3OC_6H_5$) and also phenetole ($C_2H_5OC_6H_5$), despite the possibility of competitive α-H or β-H elimination in the case of the latter.[39] The propensity of the {(Tp′)Ir(C_6H_5)$_2$} fragment (which, moreover, catalyzes the H/D exchange between C_6D_6 and a variety of organic and organometallic molecules containing C–H bonds of different types) has recently also been used to activate the α-C–H bonds of aliphatic methyl ethers CH_3OR (R = n-C_4H_9, t-C_4H_9, CH_2CH_2OMe), yielding dihydrido oxocarbene complexes **49a–c** and benzyl ethers $C_6H_5CH_2OR$.[40] As shown in Scheme 15, the overall reaction involves the participation of two molecules of the methyl ether and one of benzene per molecule of the metal precursor. Coordinatively unsaturated alkoxymethyl iridium species [(Tp′)Ir(C_6H_5)(CH_2OR)] and coordinatively saturated monohydrido oxocarbene derivatives [(Tp′)IrH(C_6H_5){=C(H)OR}] similar to **34** (Scheme 11) are intermediates in this process. The alkoxymethyl compounds [(Tp′)Ir(C_6H_5)(CH_2OR)] can be trapped upon addition of acetonitrile to yield the 1:1 adducts [(Tp′)Ir(C_6H_5)(CH_2OR)(NCMe)], which undergo thermal decomposition to give the monohydrido oxocarbenes [(Tp′)IrH(C_6H_5){=C(H)OR}]. Heating solutions of the oxocarbene complexes [(Tp′)IrH(C_6H_5){=C(H)OR}] (R = n-C_4H_9 or CH_2CH_2OMe) in cyclohexane at 80 °C gives the aryl hydrido compounds [(Tp′)IrH{κ^2(C,O)-$C_6H_4CH_2OR$}] via C–H bond cleavage and C–C coupling. The complexes have been characterized by spectroscopic techniques and, in the case of R = n-C_4H_9, by X-ray crystallography.[40b] The dihydrido complex **49b** reacts in a solvent mixture of benzene and methyl n-butyl ether at 100 °C to furnish the hydrido carbonyl n-propyl derivative **50**. This is an exceptional reaction, as CH_3–OR bond cleavage is usually considered to be energetically more demanding than C–H activation.[40b]



Scheme 15. [Ir] is the tris(3,5-dimethylpyrazol-1-yl)hydroborate Ir^{III} fragment; **49a**: R = tBu, **49b**: R = nBu, **49c**: R = CH_2CH_2OMe.

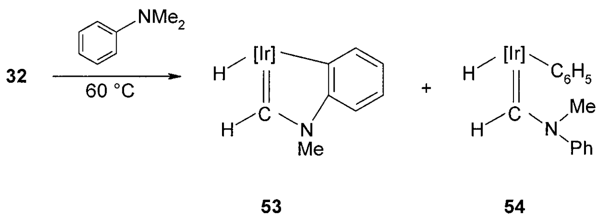
Another reaction of the 16-electron fragment [(Tp′)Ir(C_6H_5)$_2$] that involves a double α-C–H bond activation is also worth noting. Carmona et al. found that when the labile adduct **32** was treated with 2-ethylphenol in cyclohexane at 60 °C, a carbene complex **51** was formed as the major product (Scheme 16).[41] Compound **51** is probably formed by the coordinatively unsaturated intermediate [(Tp′)Ir(C_6H_5)(O-2-C_6H_4Et)], which is generated by loss of N_2 from **32** and acid-induced cleavage of one of the Ir–C_6H_5 bonds. This step is then followed by a facile double α-C–H bond activation of the ethyl group. Monitoring the reaction by NMR spectroscopy under kinetic control revealed that along with **51**, the olefin–hydrido isomer **52** is also formed, which derives from β- instead of α-H elimination from the intermediate [(Tp′)Ir(C_6H_5)(O-2-C_6H_4Et)]. Although **52** amounts to only about 5 % of the total reaction product, it could be separated from **51** and isolated after column chromatography. Using C_6D_{12} as solvent, it was confirmed that in the temperature range of 90–130 °C, an equilibrium between the two isomers exists, with a equilibrium constant K_{eq} of about 8 in favor of **51**. Theoretical calculations supported the mechanism explaining the isomerization of **51** to **52** and vice versa.[41] The remarkable feature is that whereas the conversion of metal carbenes into the corresponding olefin metal isomers is well documented, the reverse transformation is a rarely observed process and known only for a few electron-poor transition metal complexes.[42]



Scheme 16. For HBN_3, see Scheme 9.

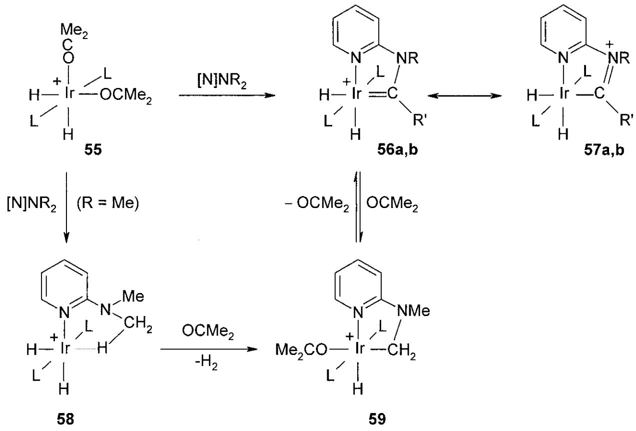
Along with the preparation of Fischer-type oxocarbenes from cyclic and non-cyclic ethers as substrates, double α-C–H bond activation of NCH_3 units of tertiary amines has also been achieved. The first example of this type of reaction was found in our laboratory in 1992 and involved the conversion of the aminophosphine $i\mathrm{Pr}_2PCH_2CH_2NMe_2$ into the corresponding secondary aminocarbene $i\mathrm{Pr}_2PCH_2CH_2N(Me)CH$: in the coordination sphere of osmium(II).[19] As mentioned above (Scheme 7), the exceptionally stable chelate complex **21** was obtained from [$OsCl_2(PPh_3)_3$] and the functionalized phosphine $i\mathrm{Pr}_2PCH_2CH_2NMe_2$ in good yield. Somewhat later, the related transformation of N,N-dimethylaniline to a chelated and also to a non-chelated aminocarbene ligand was reported by Carmona et al. Treatment of the isoprene derivative **45** (Scheme 14) with N,N-dimethylaniline led to the formation of two isomers in a ratio of about 2:1. The structure of the major isomer **53** was substantiated by X-ray crystallography.[37a] With **32** as starting material and benzene as solvent, the reaction with N,N-dimethylaniline furnished, along with **53**, the non-cyclic aminocarbene **54**, which has an intact Ir–C_6H_5 bond (Scheme 17).[37b] The observation that the chelate complex **53** is not converted into the phenyl-iridium derivative **54** when heated in benzene revealed that the two products are formed by different reaction pathways.

With 2-dimethylamino- and 2-diethylaminopyridine as precursors, Crabtree et al. also achieved a double C–H bond activation of a NCH_3 and of a NCH_2Me group attached to a six-membered ring. Reaction of the dihydrido iridium(III)



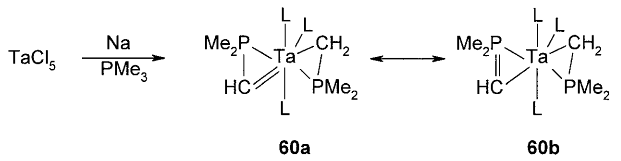
Scheme 17. [Ir] is the tris(3,5-dimethylpyrazol-1-yl)hydroborate iridium(III) fragment.

cation **55** with 2-$NC_5H_4NR_2$ (R = CH_3, C_2H_5) in CH_2Cl_2 at 25 °C afforded the chelate complexes **56a,b** in excellent yield.[43] In contrast to the reactions leading to **21**, **53**, and **54**, no elevated temperatures are required for the transformation of the alkyl group into the carbene unit. The X-ray structure analysis of **56b** showed Ir–C and C–N bonds that are longer than expected for a Ir=C double bond and shorter than expected for a C–N single bond. This indicates that the resonance form **57a,b**, generally preferred for Fischer-type carbenes,[44] must be taken into account. Notably, almost identical M–C and C–N bond lengths are found in the aminocarbene osmium and iridium complexes **23** and **53**, as in **56b**. With regard to the mechanism of the reaction shown in Scheme 18 (with R = Me), NMR studies showed that, after the acetone molecules of **55** were replaced by the aminopyridine, the labile intermediate **58** with an agostic Ir⋯H–CH_2 bond is generated. In CD_2Cl_2 at 0 °C, **58** is completely converted into **56a** after 40 minutes. In the process of forming **56a**, the alkyl hydrido derivative **59** is formed, which could be isolated after the carbene **56a** was dissolved in acetone. Compound **59** has been characterized by X-ray crystallography. Dissolving the alkyl hydrido compound **59** in CD_2Cl_2 at room temperature produces the carbene **56a** within seconds. Under the given conditions, the ratio **59**:**56a** is about 1:1. The equilibrium can be shifted in favor of **59** by addition of acetone. This work thus provides an example for a reversible α-H elimination, which is a rarely observed process,[30] but which is surprisingly facile in Crabtree's iridium system.[43]



Scheme 18. L = PPh_3; $[N]NR_2$ = 2-$NC_5H_5NR_2$; **56a**,**57a**: R = Me, R′ = H; **56b**,**57b**: R = Et, R′ = Me.

Prior to the work on such aminocarbene complexes as **21**, **23–25**, **53**, **54**, and **56a,b** formed by double α-C–H bond activation, a resonance form suggested for **57a,b** has also been proposed for the tantalum compound **60** (Scheme 19). As part of their studies on the chemistry of highly electron-rich systems of the general type $[M(PMe_3)_n]$, where M is an electron-poor transition metal, Green et al. prepared the very air- and water-sensitive compound **60** from $TaCl_5$ and sodium sand in neat PMe_3 and confirmed the molecular structure crystallographically.[45] Apart from the η^2-CH_2PMe_2 ligand, which was characterized in various transition metal complexes previously, the η^2-$CHPMe_2$ unit was unknown. The HC–PMe_2 bond in **60** is 0.13 Å shorter than the mean P–CH_3 bonds, which suggests some C–P multiple bonding similar to that of the C–N group in the osmium and iridium aminocarbene derivatives. Later, a tantalum derivative of composition $[(C_5H_5)Ta(H)_2(PMe_3)(\eta^2\text{-}CHPMe_2)]$, containing the same strained three-membered M-C-P ring found in **60**, was reported by Gibson et al. and was also characterized by an X-ray structure analysis.[46]

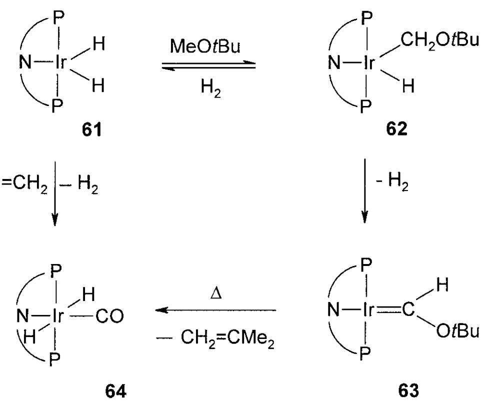


Scheme 19. L = PMe_3.

5. The Atom- and Group-Transfer Metathesis

The studies by Bergman and Carmona in particular have shown that non-cyclic methyl and ethyl ethers undergo a double α-C–H bond activation in the coordination sphere of iridium atoms to give Fischer-type oxocarbene complexes. However, some recent papers by Whited and Grubbs go an important step further and illustrate a unique mode of reactivity for those metal oxocarbenes. The initial starting material for this work was the dihydride **61**, which contains the PNP pincer ligand that is a well-known tool in transition metal chemistry, and in particular through Ozerov's extensive work.[47]

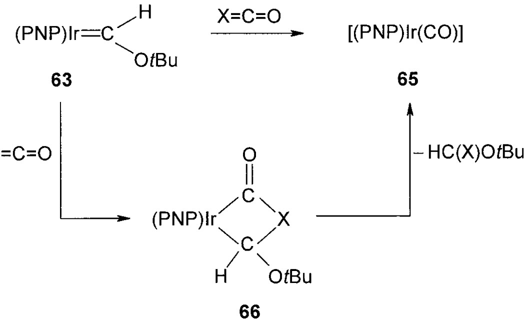
In 2008, Whited and Grubbs reported that complex **61** reacts cleanly with norbornene (acting as dihydrogen acceptor) in methyl *tert*-butyl ether at room temperature to generate a long-lived intermediate,[48] which is assumed to be the alkyl hydrido iridium(III) compound **62** formed by C–H oxidative addition at the metal (Scheme 20). Computational and mechanistic studies support this proposal.[49,50] Two equivalents of norbornene are necessary to ensure complete conversion of **61** into **63** because regeneration of **61** occurs readily upon exposure of **62** to H_2. The X-ray crystal structure analysis of **63** confirmed the square-planar coordination sphere around iridium and revealed an Ir–C bond that has nearly the same length as in **49b**.[40b] Thermolysis of **63** in C_6D_6 resulted in the formation of the octahedral dihydrido iridium-



Scheme 20. The tridentate chelate ligand is the anion $[N(4\text{-Me-2-P}i\text{Pr}_2\text{-C}_6\text{H}_3)_2]^-$.

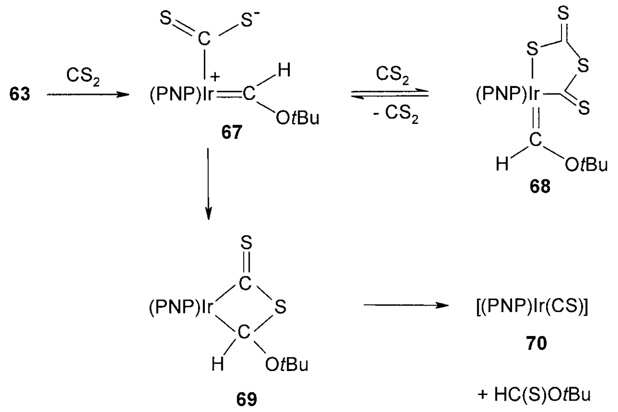
(III) carbonyl **64** with concomitant elimination of isobutene. Compound **64** was also obtained upon treatment of **61** with formaldehyde by loss of H_2. Although an analogue of the iridium oxocarbene **63** with the PCP pincer ligand first prepared by Grubbs et al. is as yet unknown, the counterpart of **64** with this chelating ligand was generated by heating a mixture of the chloro hydrido compound [(PCP)Ir(H)Cl] and NaO*t*Bu in MeO*t*Bu at 70 °C.[51]

Apart from the conversion of **63** into **64**, the most striking reactions of the iridium oxocarbene **63** are those with CO_2 and their analogues COS, PhNCO, CS_2, and PhNCS, which is a form of atom or group transfer without predecent.[48,52,53] Whited and Grubbs first found that exposure of a solution of **63** in C_6D_6 to an atmosphere of CO_2 resulted in the quantitative formation of the iridium(I) carbonyl **65** (Scheme 21).[48] *Tert*-butyl formate was identified as a byproduct. Reaction of **63** with $^{13}CO_2$ afforded $[(PNP)Ir(^{13}CO)]$, thus confirming that the carbonyl ligand is derived from CO_2. Carbonyl sulfide and phenyl isocyanate reacted similarly and effected sulfur and nitrene transfer to the carbene to generate *tert*-butyl thioformate and *N*-phenyl-*tert*-butylformimidate, respectively, and, as before, **65**. The mechanism of the reaction involves a nucleophilic attack at the heterocumulene by the d^8 metal center as the initial step, followed by cyclization to form the four-membered metallacycle **66**, similar to the formation of a metallacyclobutane as an intermediate in olefin metathesis.[54] Subsequent elimination of HC(X)O*t*Bu results in an atom- or group-transfer metathesis from the heterocumulene to the carbene ligand. When the reaction was monitored by ^{1}H NMR spectroscopy at −60 °C, signals were observed that could be assigned to the four-membered metallacycle. Computational[49] and kinetic studies[48a] were consistent with the proposed mechanism; the kinetic studies revealed that the rate of the reaction to afford **65** and HCO_2tBu is first order in both **63** and CO_2. Interestingly, the DFT calculations also rationalize the selective cleavage of the C–S and C–N bonds in SCO and PhNCO, which is attributed to the strength/weakness of the σ and π components of the respective C–X double bonds.[49]



Scheme 21. X = O, S, NPh; the tridentate chelate ligand is the anion $[N(4\text{-Me-2-P}i\text{Pr}_2\text{-C}_6\text{H}_3)_2]^-$.

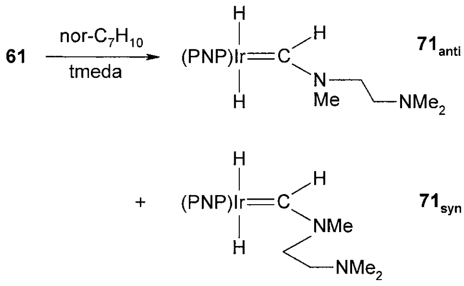
The reactivity outlined in Scheme 21 is not limited to CO_2, COS, and PhNCO. Shortly after the first communication appeared,[48] Whited and Grubbs showed that the oxocarbene complex **63** also reacted with heterocumulenes possessing no oxygen atoms, such as CS_2 and PhNCS.[55] The reaction of **63** with CS_2 did not lead to [(PNP)Ir(CS)], as would be anticipated by analogy with CO_2 (see Scheme 21), but rather to the unusual metallacyclic compound **68** (Scheme 22).[56] Compound **68** contains a head-to-tail dimer of CS_2 as part of the five-membered ring, as confirmed by an X-ray diffraction analysis. Heating a solution of **68** in benzene at 70 °C caused quantitative degradation of **68** to the expected iridium thiocarbonyl **70** with concomitant formation of *tert*-butyl thioformate and CS_2. Clearly, **68** is the kinetic product, and **70** and HC(S)O*t*Bu are the thermodynamic products of the interaction of **63** with CS_2. The common intermediate is assumed to be the zwitterion **67**, which is formed by nucleophilic attack of iridium(I) at the electrophilic heterocumulene carbon atom. With an excess of CS_2, **67** can be trapped by a second molecule of the heterocumulene to give **68**, whilst by using equivalent amounts of **63** and CS_2, the zwitterion cyclizes to the metalla(dithio)lactone **69** and then converts into the thiocarbonyl complex **70**. Additional experimental and computational studies are in agreement with this mechanism.[55]



Scheme 22. The tridentate chelate ligand is the anion $[N(4\text{-Me-2-P}i\text{Pr}_2\text{-C}_6\text{H}_3)_2]^-$.

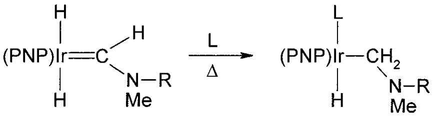
The course of the reaction of **63** with phenyl isothiocyanate is more complex, and, depending on the conditions, can lead to different products.[55] In a dilute solution of **63** in benzene, the carbene complex reacts with one equivalent of PhNCS by sulfur atom transfer to afford [(PNP)Ir(CNPh)] and *tert*-butyl thioformate HC(S)O*t*Bu. With an excess (2–10 equiv) of PhNCS, an analogue of the metallaheterocycle **68** is probably generated, which however decomposes quickly to the isonitrile derivative [(PNP)Ir(CNPh)], HC(S)O*t*Bu, and PhNCS. Treatment of [(PNP)Ir(CNPh)] with a large excess of CS_2 furnished a compound that can be formulated as the C_2S_4 adduct of the isonitrile complex, which is analogous to the CS_2 dimer **68**. Thus, **63** and [(PNP)Ir(CNPh)] behave similarly, underlining the isoelectronic relationship between these molecules.[55]

Three other recent achievements of Whited and Grubbs should also be mentioned. First, they showed that the above-mentioned dihydride **61** performs the selective double α-C–H activation of methylamines to afford dihydrido iridium(III) aminocarbenes.[57] A representative example is shown in Scheme 23. The reaction of **61** and norbornene in a 1:1 ratio with tmeda as solvent produced, along with norbornane, the six-coordinate complex **71**. Two atropisomers, *syn* and *anti*, are formed of which the latter, having the CH_3 group of the aminocarbene unit parallel to the Ir=C bond, is thermodynamically preferred. This reactivity of **61** is in sharp contrast to the dehydrogenation of MeO*t*Bu by the same system (Scheme 20), where H_2 is lost to give the square-planar oxocarbene iridium(I) species **63**. The X-ray diffraction analysis of $\mathbf{71}_{\mathbf{anti}}$ revealed a longer Ir–C bond compared with **63** and a shorter N–C bond, indicating, in analogy to **56a**,**b**/**57a**,**b**, a significant π component in this bond.[57] *N*-Methylmorpholine behaves in a similar fashion to tmeda, and upon addition to a solution of **61** affords an octahedral dihydrido iridium(III) carbene by double α-C–H bond activation. Thermolysis of $\mathbf{71}_{\mathbf{syn}}/\mathbf{71}_{\mathbf{anti}}$ results in the partial isomerization from the *trans*- to the *cis*-dihydrido iridium carbene derivatives, and both *syn* and *anti* isomers are observed to form also in this case. Prolonged thermolysis of the *cis*-dihydrido species does not lead to loss of H_2, even in the presence of norbornene.



Scheme 23. The tridentate chelate ligand is the anion $[N(4\text{-Me-2-P}i\text{Pr}_2\text{-C}_6\text{H}_3)_2]^-$.

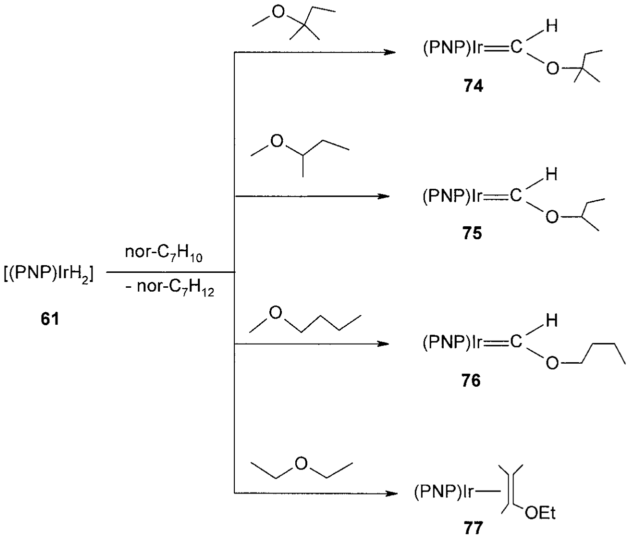
Taking into account that the dihydrido iridium(III) complex **71** possesses an 18-electron configuration and has no vacant coordination site, it is not surprising that, in contrast to **63**, it does not react with CO_2, even under forcing thermal conditions. However, heating a solution of **71** in benzene in the presence of PMe_3 led, via a phosphine-induced 1,2-hydride migration from iridium to the carbene carbon atom, to the formation of the alkyl hydrido iridium(III) compound **72** (Scheme 24). The analogous carbonyl complex **73** was obtained by thermolysis of **71** under a CO atmosphere. Given the coordinatively saturated nature of **71** and the *trans* to *cis* isomerization of the atropisomers $\mathbf{71}_{\mathbf{syn}}/\mathbf{71}_{\mathbf{anti}}$ at elevated temperature, it seems plausible that the 1,2-hydride migration precedes the association of PMe_3 and CO at the metal atom.[57]



71 **72** : L = PMe_3
73 : L = CO

Scheme 24. $R = CH_2CH_2NMe_2$; the tridentate chelate ligand is the anion $[N(4\text{-Me-2-P}i\text{Pr}_2\text{-C}_6\text{H}_3)_2]^-$.

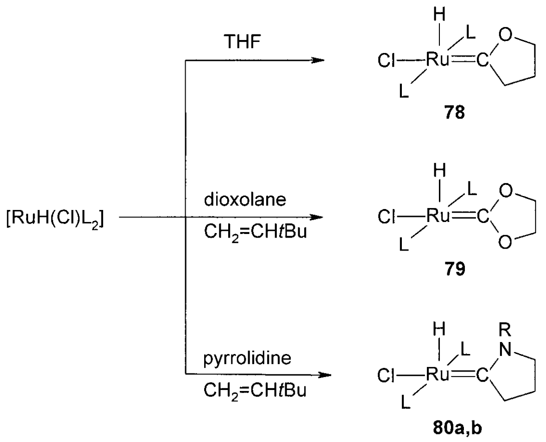
The second noteworthy result, published in late 2009, is the interaction of the {(PNP)Ir} fragment with a series of non-cyclic and cyclic ethers.[50] With the dihydrido complex **61** and methyl ethers as precursors, and in the presence of norbornene, four-coordinate oxocarbene–iridium(I) complexes that are structurally related to **63** are obtained (**74**–**76**; Scheme 25). The high selectivity with which these metal carbenes are formed is remarkable, in particular for methyl *n*-butyl ether as the substrate. The reaction of **61** with norbornene in THF at 60 °C resulted in the formation of the thermally stable complex [(PNP)Ir{=CO(CH$_2$)$_3$}], which contains the same cyclic carbene ligand found in **29** and **32.** Under milder conditions, the six-coordinate intermediate [(PNP)Ir(H)$_2${=CO(CH$_2$)$_3$}] with *trans*-disposed hydrido ligands had been observed and characterized by ^{1}H and



Scheme 25. The tridentate chelate ligand is the anion $[N(4\text{-Me-2-P}i\text{Pr}_2\text{-C}_6\text{H}_3)_2]^-$.

^{31}P NMR spectroscopy. Regarding the structure, it is a relative of the dihydrido iridium aminocarbene **71**. With diethyl ether as the reagent and in the presence of norbornene, compound **61** reacts slowly to afford the ethyl vinyl ether complex **77**. This divergent behavior with respect to THF and Et_2O resembles that observed for Bergman's [(C_5Me_5)(PMe_3)Ir] system (Scheme 12), which also gives an ethyl vinyl ether adduct by α,β-dehydrogenation of diethyl ether.[31]

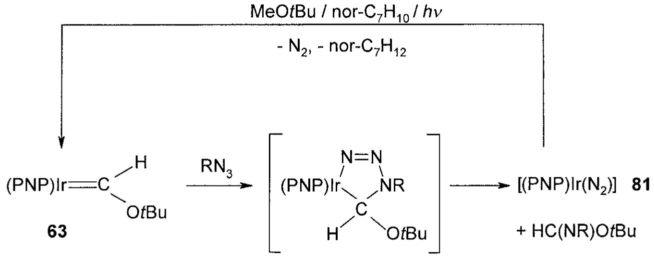
In contrast to diethyl ether and THF, the reaction of **61** with norbornene in 1,4-dioxane resulted in a single C-H oxidative addition to the (PNP)Ir intermediate to yield the iridium(III) complex [(PNP)IrH(1,4-dioxan-2-yl)]. This complex could be trapped with CO to afford a stable 1:1 adduct that is structurally related to the alkyl hydrido carbonyl derivative **73**.[50] These studies supplement previous work by Caulton et al. on the reactivity of four-coordinate [RuH(Cl)($P\mathit{i}Pr_3$)$_2$]. This 14-electron species, generated from the corresponding dimer, reacted with THF, dioxolane, and pyrrolidine to give the five-coordinate ruthenium(II) complexes **78, 79**, and **80 a,b**, which contain cyclic oxo- and aminocarbene ligands (Scheme 26).[58,59] The six-membered counterparts 1,4-dioxane, 1,3,5-trioxane, and piperidine did not react similarly and failed to produce the ruthenium carbene compounds upon reaction with [RuH(Cl)($P\mathit{i}Pr_3$)$_2$]$_2$. An analogue of **80 a** with PCy_3 instead of $P\mathit{i}Pr_3$ as phosphine ligand was obtained from [RuH(H_2)Cl(PCy_3)$_2$] and excess pyrrolidine in the presence of CH_2=CH*t*Bu.[58b]



Scheme 26. **80 a**: R = H, **80 b**: R = Me; L = P*i*Pr$_3$.

Caulton's extensive work on the reactivity of oligohydrido osmium(IV) complexes [$OsH_{4-n}Cl_n$($P\mathit{i}Pr_3$)$_2$], of which the representative with $n=2$ was first prepared in our laboratory,[16g,60] revealed that the osmium counterpart of the ruthenium carbene **78** is also accessible. It is formed as the major product from [OsH_3Cl($P\mathit{i}Pr_3$)$_2$] and CH_2=CH*t*Bu (ratio 1:2) in neat THF, and it has been characterized by ^{1}H and ^{31}P NMR spectroscopy.[58] The reaction of [OsH_3Cl($P\mathit{i}Pr_3$)$_2$] with pyrrolidine in benzene at room temperature leads to the rapid formation of a 1:1 adduct, which releases H_2 over a period of 3 days and converts into the five-coordinate intermediate [OsHCl{N(H)C_4H_8}($P\mathit{i}Pr_3$)$_2$]. This species reacts intramolecularly by double α-C−H bond activation at the coordinated pyrrolidine to give the seven-coordinate osmium(IV) complex [OsH_3Cl{=CN(H)(CH_2)$_3$}($P\mathit{i}Pr_3$)$_2$] that contains a cyclic five-membered aminocarbene ligand. The formation of this complex from the pyrrolidine adduct [OsH_3Cl{N(H)C_4H_8}($P\mathit{i}Pr_3$)$_2$] proceeds at the same rate in the presence of CH_2=CH*t*Bu as a potential H_2 scavenger, which is presumably due to the fact that both trishydrido osmium(IV) compounds have no free coordination site to bind the olefin. The reaction of [OsH_2Cl_2($P\mathit{i}Pr_3$)$_2$] with pyrrolidine in a ratio of 1:4 occurs analogously to the trishydrido chloro compound [OsH_3Cl($P\mathit{i}Pr_3$)$_2$] and affords the carbene complex [OsH_3Cl{=CN(H)(CH_2)$_3$}($P\mathit{i}Pr_3$)$_2$] and pyrrolidinium chloride as a byproduct. A competition experiment resulted in the surprising observation that the reaction of equimolar amounts of [OsH_2Cl_2($P\mathit{i}Pr_3$)$_2$] and pyrrolidine in neat THF furnishes exclusively the aminocarbene [OsH_3Cl{=CN(H)(CH_2)$_3$}($P\mathit{i}Pr_3$)$_2$], with none of the oxocarbene [OsHCl{=CO(CH_2)$_3$}($P\mathit{i}Pr_3$)$_2$] being detected.[58]

The third recent achievement of Whited and Grubbs marks an important extension of their work on atom- and group-transfer metathesis. Taking the isoelectronic nature of CO and N_2 into account, it was found that the iridium(I) oxocarbene **63** not only reacted with isocyanates RNCO but also with organic azides RN_3.[61] These reactions resulted in quantitative nitrene group transfer to the carbene and led to the formation of the formerly unknown dinitrogen adduct **81** and a formimidate. Moreover, in accord with the isoelectronic analogy between CO_2 and N_2O, treatment of **63** with nitrous oxide gave *tert*-butyl formate and, as before, **81**. By analogy with the mechanism previously proposed by Collman to explain the formation of *trans*-[IrCl(N_2)(PPh_3)$_2$] from *trans*-[IrCl(CO)(PPh_3)$_2$] and aroyl azides,[62] Whited and Grubbs proposed that the reaction of **63** and RN_3 to give **81** proceeds by 1,3-dipolar cycloaddition to give a five-membered $IrCN_3$ iridiacycle, which is either a transition state or a short-lived intermediate (Scheme 27). Recent studies by Hillhouse, Cundari et al. on the reactivity of nickel(0) carbene complexes toward azides, leading ultimately to nickel(0) nitrenes and ketimines, support this proposal.[63] Irradiation of **81** in MeO*t*Bu at ambient temperature in the presence of norbornene led to the quantitative reconversion into **63**.[61]



Scheme 27. R = $SiMe_3$, 2,6-C_6H_3(*i*Pr)$_2$, 1-adamantyl; the tridentate chelate ligand is the anion [N(4-Me-2-P*i*Pr$_2$-C_6H_3)$_2$]$^-$.

The observation that the reaction of **81** with MeO*t*Bu to give **63** is not hampered by formimidates allowed the development of a catalytic process for the oxidation of MeO*t*Bu to HC(NR)O*t*Bu. Carefully controlled addition of 1-

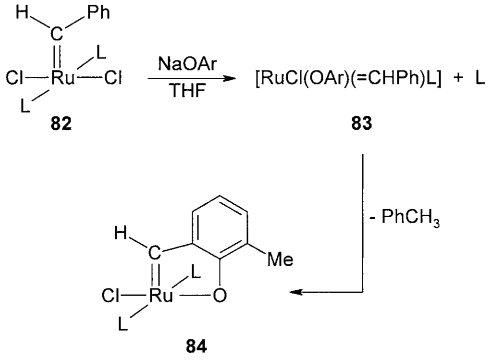
adamantyl azide to a solution of **81** (10% loading relative to the azide) and excess norbornene in methyl *tert*-butyl ether under mild photolysis gave *N*-adamantyl *tert*-butyl formimidate in high yield.[53] The isomers of MeO*t*Bu with *s*Bu and *n*Bu instead of *t*Bu could also be converted into their corresponding formimidates, albeit less efficiently.

6. Summary and Outlook

The results summarized in this Review reveal that apart from established routes, transition metal carbenes can be prepared by double α-C–H bond activation of alkane and cycloalkane derivatives containing an OR or NR_2 functionality. Moreover, the reports published by Whited and Grubbs in 2008 and 2009 indicate that the newly observed oxygen- or sulfur-atom and nitrene group-transfer metathesis reactions could supplement the well-established olefin metathesis reaction as a route to hydrocarbon functionalization. The significance of these studies was recently highlighted by the observation that the tandem double α-C–H bond activation/group transfer oxidation with methyl ethers and organic azides as substrates can be made catalytic using coordinatively unsaturated iridium complexes as catalysts. Despite the present limitations of the process, it appears possible that the experimental work by Whited and Grubbs, together with the computational studies by Yates and Cundari, may lead to predictions concerning similar reactions of electron-rich transition metal carbenes with other multiply bonded electrophiles.

Could metal-bonded carbenes be obtained by double α-C–H bond activation of alkanes and cycloalkanes that do not contain OR or NR_2 substituents at the α-carbon atom? As already mentioned, previous attempts by Fischer (and possibly also by others) to generate metal complexes of the general composition $[M(=CH_2)L_n]$ from methane as precursor failed. Although the conversion of aliphatic hydrocarbons RCH_3 such as methane into carbenes and H_2 is highly endothermic, it is nevertheless conceivable that by using appropriate transition metal compounds as starting materials, non-functionalized alkanes or cycloalkanes could be converted into coordinated carbenes.

A hint of how to succeed in this way was recently reported by Caulton et al., who observed that the reaction of the Grubbs catalyst **82** with the sodium phenolate NaO-2,6-$C_6H_3Me_2$ in THF affords at first the ruthenium compound **83** containing only one phosphine ligand (Scheme 28).[64] In solution and in the presence of PCy_3, this intermediate then evolves slowly to the five-coordinate complex **84** by transfer of two hydrogen atoms from one *ortho*-methyl group of the aryloxide to the CHPh carbene carbon atom, generating toluene as the leaving group. Regarding the mechanism of this unusual double α-C–H bond activation, Caulton et al. proposed that an agostic interaction from a sterically accessible methyl C–H bond could stabilize the coordinatively unsaturated intermediate **83**. This interaction not only holds the bulky aryloxide in position, but also allows a recoordination of the displaced phosphine and lastly favors the C–H bond cleavage. The driving force for the whole reaction, including the formation of **84**, therefore appears to be steric in origin. The elimination of toluene should provide entropic assistance for the formation of the new carbene unit. Taking this proposal into account, it could be possible, as happened similarly in Shaw's previous work,[15] to convert a nonfunctionalized CH_3 group of a hydrocarbon derivative $CH_3(CH_2)_nX$ that has a coordinating substituent X (such as F, Cl, OPh) at the end of the aliphatic chain into a carbene moiety and thus extend the scope of the atom- or group-transfer metathesis. Even the conversion of a hydrocarbon $CH_3(CH_2)_nX$ into a carbyne ligand might not be an unrealistic goal.[65]



Scheme 28. L = PCy_3; Ar = 2,6-$C_6H_3Me_2$.

Received: January 18, 2010

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[11] It should be noted that there are two systems of nomenclature for compounds with metal–carbon double bonds. In contrast to Fischer, who named any unit of the general composition C(R)R′ a carbene, regardless of whether or not R or R′ contains a heteroatom such as oxygen, sulfur, or nitrogen, Schrock preferred the name alkylidene in cases where R and R′ are either hydrogen, an alkyl, aryl, or trimethylsilyl group. Schrock argued that a primary alkylidene CHR is derived from a primary alkyl ligand CH_2R and a secondary alkylidene CR_2 from a secondary alkyl ligand CHR_2. Although both terms—carbene and alkylidene—occur as synonyms in the literature, herein only the term carbene is used.

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