Reviews

Half-Sandwich-Type Complexes with Non-Fischer-Type Carbene Ligands: Synthesis, Molecular Structure, Substitution, and C−C Coupling Reactions[†]

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Half-sandwich-type complexes with non-Fischer-type carbene ligands and rhodium, iridium, ruthenium, and osmium as the metal centers are accessible by two routes. While the rhodium and iridium η^5-cyclopentadienyl and η^5-indenyl compounds with Rh=CRR′ and Ir=CRR′ as the molecular fragments are prepared from starting materials that already contain the carbene ligand, the related ruthenium η^5-cyclopentadienyl and η^5-indenyl complexes as well as the corresponding osmium η^6-arene derivatives are obtained from half-sandwich-type precursors which react with a diazoalkane to give the metal carbene. The reactions of the rhodium and iridium compounds $[(\eta^5\text{-}C_5H_5)M(=CRR')(L)]$ (M = Rh, Ir) and $[(\eta^5\text{-}C_9H_7)Rh(=CRR')(L)]$ with Lewis bases and acids result not only in ligand substitution, sometimes accompanied by C−C coupling, but also in migratory insertion of the CRR′ unit into one of the C−H bonds of the cyclopentadienyl or indenyl ring. The ruthenium complexes $[(\eta^5\text{-}C_5H_5)RuCl(=CRR')(L)]$ and $[(\eta^5\text{-}C_9H_7)RuCl(=CRR')(L)]$ readily react with Grignard reagents and organolithium compounds by displacement of the chloride and subsequent C−C coupling to yield half-sandwich complexes with η^3-allyl, η^3-benzyl, and substituted olefins as ligands. The reactivity of the osmium arene carbenes $[(\eta^6\text{-mes})OsX_2(=CR_2)]$ is highlighted by the observation that treatment of these complexes with water in acetone solution transforms the $OsX_2(=CR_2)$ fragment into an $OsR_2(CO)$ moiety.

Introduction

It was soon after the serendipitous preparation of ferrocene, $[Fe(\eta^5\text{-}C_5H_5)_2]$, and the elucidation of its sandwich-type structure that the first transition-metal complexes of the general composition $[(\eta^5\text{-}C_5H_5)M(L)_n]$ were prepared. Since the metal atom in these compounds is enclosed on only one side by a disklike ring ligand but is coordinated with conventional ligands on the other side, the structure appeared to be reminiscent of a half-sandwich. In pioneering work by both the Fischer and Wilkinson groups the conventional ligands L were mainly CO,[1,2] while in subsequent studies other ligands such as NO, halides, isocyanides, olefins, and phosphines also have been used. Moreover, instead of C_5H_5 similar planar ring systems such as C_4H_4, C_6H_6, C_7H_7, and C_8H_8 and their substituted congeners were equally employed.[3]

Our own interest in the chemistry of half-sandwich-type complexes was due to an unusual observation. In the course of a systematic investigation of the reactivity of low-valent, electron-rich transition-metal compounds, we found that the cobalt complex $[(\eta^5\text{-}C_5H_5)Co(PMe_3)_2]$ can be protonated even by weak acids such as NH_4^+ to form the cation $[(\eta^5\text{-}C_5H_5)CoH(PMe_3)_2]^+$, which is quite stable and can be isolated as the PF_6^- or BF_4^- salt.[4] In contrast, the dicarbonyl counterpart $[(\eta^5\text{-}C_5H_5)CoH(CO)_2]^+$, thought to be generated from $[(\eta^5\text{-}C_5H_5)Co(CO)_2]$ and CF_3CO_2H,[5] is exceedingly labile and even in acidic media decomposes quite rapidly. The behavior of $[(\eta^5\text{-}C_5H_5)Co(PMe_3)_2]$ turned out to be not unique, and thus not only the rhodium analogue $[(\eta^5\text{-}C_5H_5)Rh(PMe_3)_2]$ but also the structurally related ruthenium and osmium arene complexes $[(\eta^6\text{-}C_6R_6)M(PMe_3)_2]$ (M = Ru, Os) react with acids HX to give the corresponding hydrido−metal cations.[6] Even “mixed-ligand” compounds of the type $[(\eta^n\text{-}C_nR_n)M(L)(L')]$ (see Chart 1) can be protonated or alkylated, provided that at least one

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[†] Dedicated to Professor Luis A. Oro, in recognition of his widespread and creative work in organometallic chemistry.

(1) Fischer, E. O.; Fritz, H. P. *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 56−115.

(2) Wilkinson, G.; Cotton, F. A. *Prog. Inorg. Chem.* **1959**, *1*, 1−124.

(3) (a) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986; Chapter 4. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapter 3.7. (c) Elschenbroich, E. *Organometallchemie*, 4th ed.; Teubner: Stuttgart, Germany, 2003; Chapter 15.4.

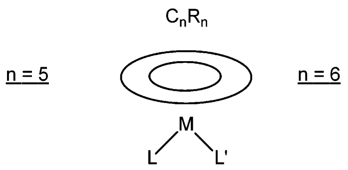
(4) Werner, H.; Hofmann, W. *Chem. Ber.* **1977**, *110*, 3481−3493.

(5) Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653−3666.

(6) Review: Werner, H. *Angew. Chem.* **1983**, *95*, 932−954; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927−949.

10.1021/om049122g CCC: $30.25

Chart 1. Half-Sandwich-Type Complexes with Electrophilic Metal Centers



M = Co, Rh, Ir	M = Ru, Os
L = L' = PR_3, $P(OR)_3$	L = L' = PR_3, $P(OR)_3$
L = PR_3, L' = PR'_3, $P(OR)_3$, CO, CS, CNR, C_2H_3R	L = PR_3, L' = PR'_3, $P(OR)_3$, CO, CNR, C_2H_3R

of the ligands C_nR_n, L, and L′ possesses well-defined donor properties. This reactivity can be qualitatively understood since, according to MO calculations by Hoffmann and Albright,[7] half-sandwich-type complexes $[(\eta^n\text{-}C_nR_n)M(L)_2]$ have an energetically high-lying molecular orbital which is nonbonding with respect to the metal−ligand bonds and resembles in its "shape" the d_{z^2} orbital of the metal in a planar d^8 system. Thus, the half-sandwich-type complexes $[(\eta^n\text{-}C_nR_n)M(L)(L')]$ and the Vaska-type compounds *trans*-$[IrX(CO)(PR_3)_2]$ are near-relatives and can both be regarded as metal bases.[6,8]

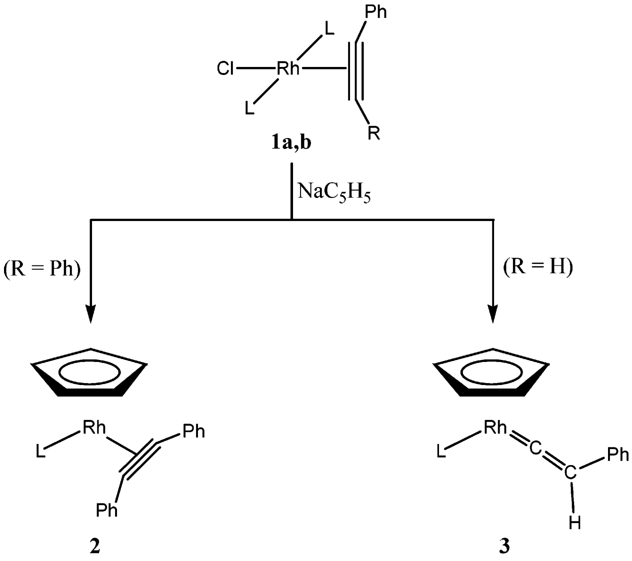
Following the preparation of the alkyne complexes $[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}RC{\equiv}CR')(P\textit{i}Pr_3)]$ (R and R′ = Me, Ph), which proved to be useful precursors for rhodium(III) vinyl and η^3-allyl derivatives,[9] we attempted to obtain also the acetylene counterpart $[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}C_2H_2)(P\textit{i}Pr_3)]$ but failed. Treatment of *trans*-$[RhCl(\eta^2\text{-}C_2H_2)(P\textit{i}Pr_3)_2]$ with NaC_5H_5 gave, quite unexpectedly, the half-sandwich-type vinylidene compound $[(\eta^5\text{-}C_5H_5)Rh({=}C{=}CH_2)(P\textit{i}Pr_3)]$ instead of the rhodium alkyne isomer. The phenylacetylene derivative **1b** reacted analogously and with NaC_5H_5 afforded the phenylvinylidene complex **3** (Scheme 1).[10]

These observations, together with the rich chemistry offered by both $[(\eta^5\text{-}C_5H_5)Rh({=}C{=}CH_2)(P\textit{i}Pr_3)]$ and **3**,[11] raised the questions whether the carbene analogues $[(\eta^5\text{-}C_5H_5)Rh({=}CRR')(P\textit{i}Pr_3)]$ also are accessible and what their reactivity toward nucleophiles and electrophiles might be. The work, which we started in the mid 1990s, finally led us to explore the field of half-sandwich-type complexes with Rh(=CRR′), Ir(=CRR′), Ru(=CRR′), and Os(=CRR′) units as molecular building blocks, and the results of this exploration will be described in this account.

The Multifaceted Chemistry of Half-Sandwich-Type Rhodium Carbenes

The beginning of our work in this field was defined by attempts to prepare square-planar rhodium(I) carbene complexes *trans*-$[RhCl({=}CRR')(PX_3)_2]$, which were considered to be useful starting materials for the synthesis of half-sandwiches $[(\eta^5\text{-}C_5H_5)Rh({=}CRR')(PX_3)]$. To obtain these four-coordinate precursors, we reacted the rather labile ethene derivative *trans*-$[RhCl(C_2H_4)(P\textit{i}Pr_3)_2]$ (**5**) with Ph_2CN_2 and similar diazoalkanes, but instead of the carbene complexes **7a**−**c** (Scheme 2) we isolated the diazoalkane compounds *trans*-$[RhCl(N_2CRR')(P\textit{i}Pr_3)_2]$ in excellent yields.[12] The successful, but unexpected, route to the required rhodium(I) carbenes **7a**−**g** was less direct, involving in the initial step the preparation of the bis(stibine) complexes *trans*-$[RhCl({=}CRR')(Sb\textit{i}Pr_3)_2]$ (**6a**−**d**) from **4** and $RR'CN_2$ by substitution of ethene and elimination of N_2 and subsequent displacement of the two stibine ligands by two phosphines.[13] In addition to $P\textit{i}Pr_3$ other phosphines such as $P\textit{i}Pr_2Ph$, $P\textit{i}PrPh_2$, PPh_3, and PPh_2Me also could be used and, as was shown more recently, the bulky chelating bis(phosphine) 1,2-$C_2H_4(P\textit{t}Bu_2)_2$ could be employed as well.[14]

Scheme 1[a]



[a] Legend: L = $P\textit{i}Pr_3$.

While the rhodium vinylidenes *trans*-$[RhCl({=}C{=}CHR)(P\textit{i}Pr_3)_2]$ are rather inert toward cyclopentadienyllithium or -sodium, the carbene derivatives **6a**,**b** and **7a**−**g** react with NaC_5H_5 in THF at room temperature to give the half-sandwiches **8a**,**b** and **9a**−**g** in good to excellent yields.[15] The deeply colored solids are

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(7) Hoffmann, R.; Albright, T. A. Unpublished results. See: Hofmann, P. *Angew. Chem.* **1977**, *89*, 551−553; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536−537.

(8) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335−344.

(9) (a) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327−356. (b) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164−1169.

(10) (a) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem.* **1983**, *95*, 428−429; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414−416. (b) Werner, H.; Wolf, J.; Garcia Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397−411.

(11) (a) Wolf, J.; Werner, H. *J. Organomet. Chem.* **1987**, *336*, 413−428. (b) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Organomet. Chem.* **1988**, *340*, 161−178. (c) Werner, H.; Wolf, J.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1988**, *342*, 381−398. (d) Höhn, A.; Werner, H. *Chem. Ber.* **1988**, *121*, 881−886. (e) Werner, H.; Garcia Alonso, F. J.; Otto, H.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1988**, *121*, 1565−1573. (f) Brekau, U.; Werner, H. *Organometallics* **1990**, *9*, 1067−1070. (g) Werner, H.; Brekau, U.; Dziallas, M. *J. Organomet. Chem.* **1991**, *406*, 237−260.

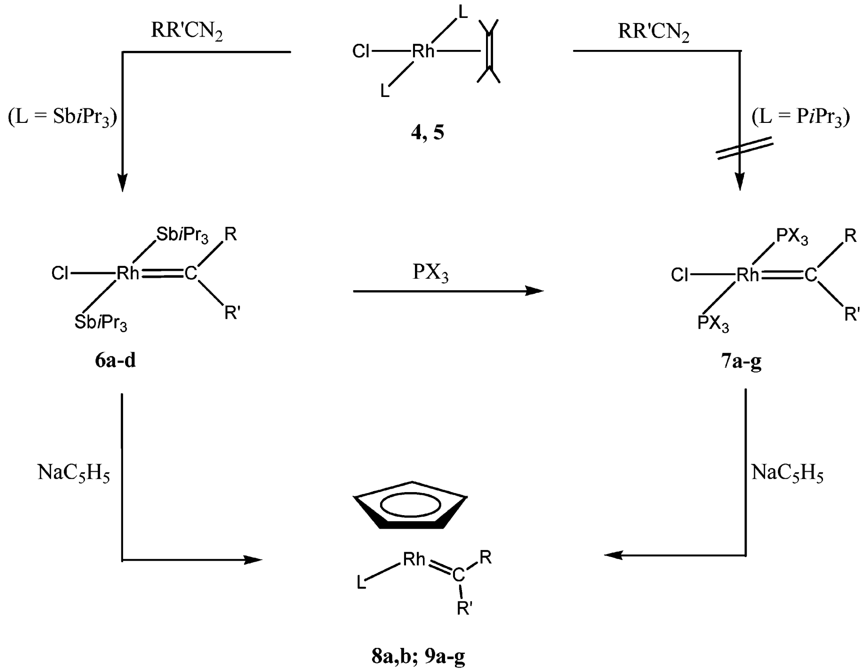
(12) (a) Wolf, J.; Brandt, L.; Fries, A.; Werner, H. *Angew. Chem.* **1990**, *102*, 584−586; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 510−512. (b) Werner, H.; Mahr, N.; Wolf, J.; Fries, A.; Laubender, M.; Bleuel, E.; Garde, R.; Lahuerta, P. *Organometallics* **2003**, *22*, 3566−3576.

(13) (a) Schwab, P.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem.* **1993**, *105*, 1498−1500; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1480−1482. (b) Werner, H.; Schwab, P.; Bleuel, E.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1997**, *3*, 1375−1384.

(14) Pechmann, T.; Brandt, C. D.; Werner, H. *Organometallics* **2003**, *22*, 3004−3006.

(15) Werner, H.; Schwab, P.; Bleuel, E.; Mahr, N.; Windmüller, B.; Wolf, J. *Chem. Eur. J.* **2000**, *6*, 4461−4470.

Scheme 2

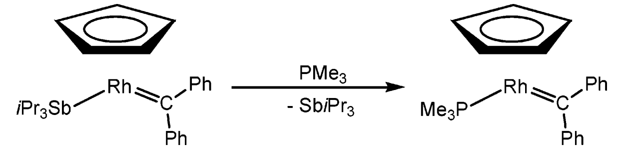


	L
4	Sb*i*Pr$_3$
5	P*i*Pr$_3$

	R	R'
6a	Ph	Ph
6b	Ph	*o*-Tol
6c	Ph	*p*-Tol
6d	*p*-Tol	*p*-Tol

	L/PX$_3$	R	R'
8a	Sb*i*Pr$_3$	Ph	Ph
8b	Sb*i*Pr$_3$	Ph	*o*-Tol
7a, 9a	P*i*Pr$_3$	Ph	Ph
7b, 9b	P*i*Pr$_3$	Ph	*p*-Tol
7c, 9c	P*i*Pr$_3$	*p*-Tol	*p*-Tol
7d, 9d	P*i*Pr$_2$Ph	Ph	Ph
7e, 9e	P*i*PrPh$_2$	Ph	Ph
7f, 9f	PPh$_3$	Ph	Ph
7g, 9g	PMePh$_2$	Ph	Ph

Scheme 3



8a **9h**

only moderately air-sensitive and are readily soluble in most common organic solvents. The ^{13}C NMR spectra of **8a**,**b** and **9a**−**g** display a resonance for the carbene carbon atom in the low-field region at δ ∼250−270, which in comparison with the resonances for the 16-electron precursors **6a**,**b** and **7a**−**g** is shifted upfield by about 45−75 ppm. Various attempts to prepare the pentamethylcyclopentadienyl compounds [(η^5-C_5Me_5)-Rh(=CPh_2)(L)] (L = Sb*i*Pr$_3$, P*i*Pr$_3$) from **6a** or **7a** and LiC_5Me_5 or NaC_5Me_5 failed.

Not only in **6a** but also in **8a** the stibine ligand is relatively weakly bound and therefore can be displaced by PMe$_3$, CO, and CN*t*Bu (Schemes 3 and 4).[15] The reactions proceed in pentane at room temperature and afford the products in ca. 85% yield. In contrast to trimethylphosphine, P*i*Pr$_3$ appears to be unable to displace the stibine ligand in **8a**, which possibly is due to the bulkiness of the attacking phosphine. The X-ray crystal structure of the carbonyl complex **10** revealed that the molecule possesses the anticipated two-legged piano-stool configuration with a Rh−CPh$_2$ distance of 1.906(3) Å. In agreement with the general bonding scheme,[16] this bond length is somewhat shorter than those in related rhodium(I) carbonyl compounds with a Fischer-type carbene ligand.[17] The trimethylsilyl-substituted complex [(η^5-$C_5H_4SiMe_3$)Rh(=CPh_2)(Sb*i*Pr$_3$)] behaves similarly to **8a** and upon treatment with PMe$_3$, CO and CN*t*Bu affords the substitution products [(η^5-$C_5H_4SiMe_3$)Rh(=CPh_2)(PMe$_3$)], [(η^5-$C_5H_4SiMe_3$)-Rh(=CPh_2)(CO)], and [(η^5-$C_5H_4SiMe_3$)Rh(=CPh_2)-(CN*t*Bu)], respectively.[18]

The reactions of **8a** with diphenyl- and di-*p*-tolyldiazomethane, undertaken to find out whether a C−C coupling between the carbene ligand and the CR$_2$ fragment of the substrate occurs, followed an unexpected route. Instead of the olefin Ph$_2$C=CR$_2$ or the bis(carbene) complex [(η^5-C_5H_5)Rh(=CPh_2)(=CR_2)], formed by substitution of Sb*i*Pr$_3$ for CR$_2$, the respective diazine R$_2$C=NN=CR$_2$ was obtained.[15] Moreover, the starting material **8a** was reisolated. To explain the mechanism

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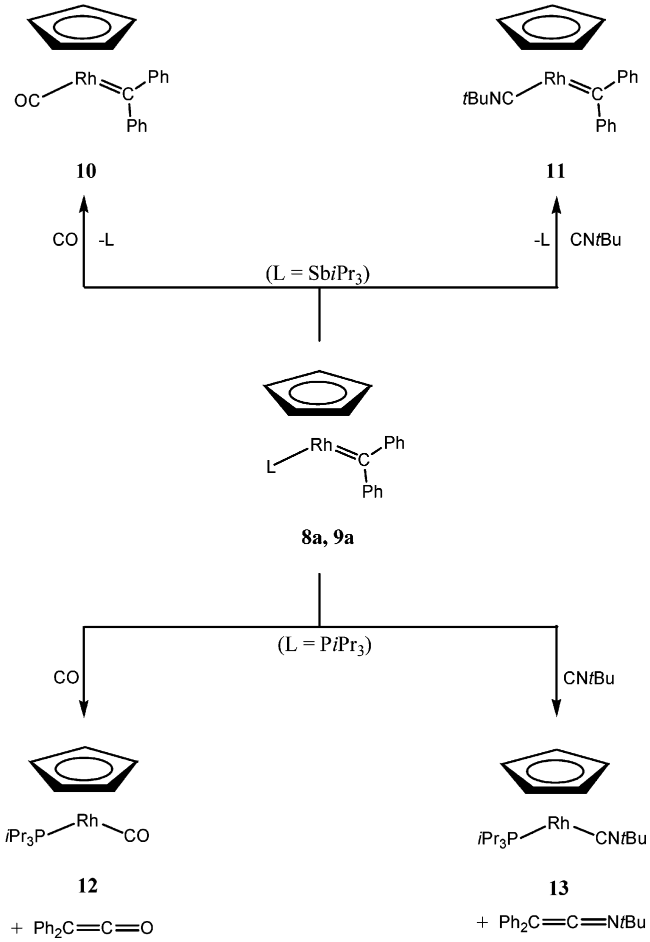
[16] Hofmann, P. In *Transition Metal Carbene Complexes;* Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, Germany, 1983; p 113.

[17] (a) Macomber, D. W.; Rogers, R. D. *J. Organomet. Chem.* **1986**, *308*, 353−360. (b) Erker, G.; Lecht, R.; Tsay, Y.-H.; Krüger, C. *Chem. Ber.* **1987**, *120*, 1763−1765. (c) Erker, G.; Mena, M.; Hoffmann, U.; Menjon, B.; Petersen, J. L. *Organometallics* **1991**, *10*, 291−298.

[18] Bleuel, E.; Werner, H. *C. R. Acad. Sci. Paris*, *Ser. IIc* **1999**, 341−349.

Scheme 4

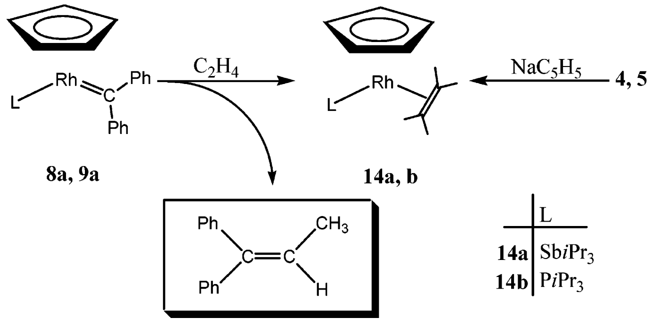


of these reactions, it is conceivable that initially a short-lived 1:1 adduct of **8a** and CR_2 is generated, which reacts with a second molecule of R_2CN_2 to give the diazine.

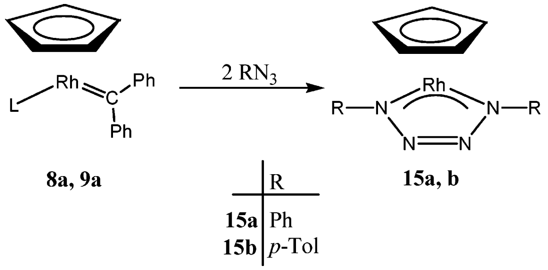
In contrast to **8a**, which upon treatment with CO and CN*t*Bu affords the carbene complexes **10** and **11** by displacement of the stibine ligand, the phosphine counterpart **9a** reacts with carbon monoxide and *tert*-butyl isocyanide to give the half-sandwich-type compounds **12** and **13** (see Scheme 4). As the organic products, diphenylketene and N-*tert*-butylketenimine are formed. We note that despite the difference in the electronic configurations between **6a** and **7a** on one hand and **8a** and **9a** on the other, the complexes **7a** and **9a** behave in a completely analogous manner toward CO and CN*t*Bu. Since tetraphenylethene, which would have been produced if free CPh_2 were generated in situ,[19] could not be detected as a byproduct in the reactions of **9a** with CO and CN*t*Bu, we assume that both the ketene and the ketenimine are formed by C−C coupling in the coordination sphere of rhodium.

Diphenylcarbene complexes **8a** and **9a** also react with ethene even at room temperature. Similarly to the reactions of **9a** with CO and CN*t*Bu, the carbene ligand is displaced, and in addition to the half-sandwiches **14a**,**b** the trisubstituted olefin $Ph_2C{=}CHCH_3$ is generated (Scheme 5). This olefin is formally built up by two carbene units, one originating from the CPh_2 moiety of

Scheme 5



Scheme 6



8a or **9a** and the other from ethene. The analogy in the course of the reactions of **8a** and **9a** is noteworthy insofar as from the four-coordinate precursors the bis(phosphine) derivative **7a** reacts with ethene to give $Ph_2C{=}CHCH_3$, while the bis(stibine) compound **6a** upon treatment with C_2H_4 affords the isomeric $CH_2{=}CHCHPh_2$ as the main coupling product.[13] To explain the formation of $Ph_2C{=}CHCH_3$ from **8a** or **9a** and ethene, we assume that in the initial stage of the reaction both the carbene CPh_2 and the olefin are coordinated to rhodium. Although the respective, probably short-lived intermediate $[(\eta^5\text{-}C_5H_5)Rh({=}CPh_2)(C_2H_4)(L)]$ (L = Sb*i*Pr$_3$, P*i*Pr$_3$) is a 20-electron species, we favor this proposal insofar as it is known that ligand substitution reactions of half-sandwich-type rhodium(I) complexes follow an associative mechanism.[20] The next step could be the formation of a metallacyclobutane, which, via a β-H shift, should afford a rhodium(III) η^3-allyl hydrido intermediate. This can react by intramolecular reductive coupling of the hydrido ligand and the less shielded CH_2 carbon atom of the allylic moiety to form the substituted olefin $Ph_2C{=}CHCH_3$.

Attempts to connect a carbene and a nitrene fragment in the coordination sphere of rhodium and generate the ketimine $Ph_2C{=}NR$ by C−N coupling led to a surprising result. If the starting materials **8a** and **9a** are treated with two equiv of RN_3 in pentane, instead of an addition of the azide or the corresponding nitrene to the metal−carbon double bond the displacement of the carbene *and* the stibine or phosphine ligands takes place. After chromatographic workup, the compounds **15a**,**b** were isolated as moderately air-stable solids in about 70% yield (Scheme 6).[15] In the presence of PhN_3, the cobalt half-sandwiches $[(\eta^5\text{-}C_5H_5)Co(CO)_2]$ and $[(\eta^5\text{-}C_5Me_5)Co(PMe_3)_2]$ behave analogously and afford the tetraazadiene complexes $[(\eta^5\text{-}C_5H_5)Co(\kappa^2\text{-}PhN_4Ph)]$ and $[(\eta^5\text{-}C_5Me_5)Co(\kappa^2\text{-}PhN_4Ph)]$, respectively.[21] The general view is that tetraazadienes possess relatively strong

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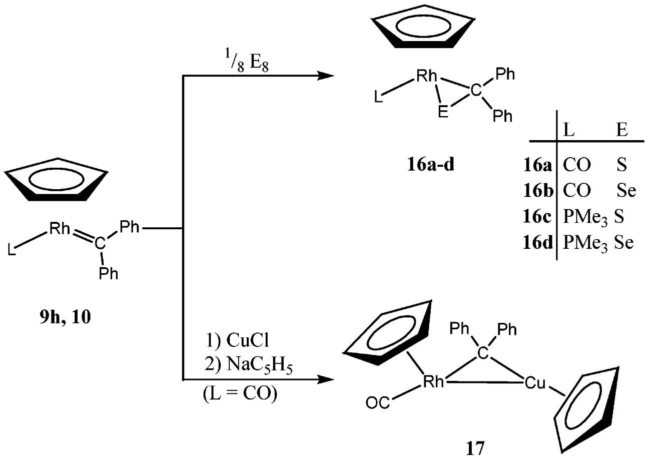
(19) Fries, A. Ph.D. Thesis, Universität Würzburg, 1993.

(20) (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657−1663. (b) Basolo, F. *Polyhedron* **1990**, *9*, 1503−1535.

Scheme 7



9h, 10

16a-d

	L	E
16a	CO	S
16b	CO	Se
16c	PMe_3	S
16d	PMe_3	Se

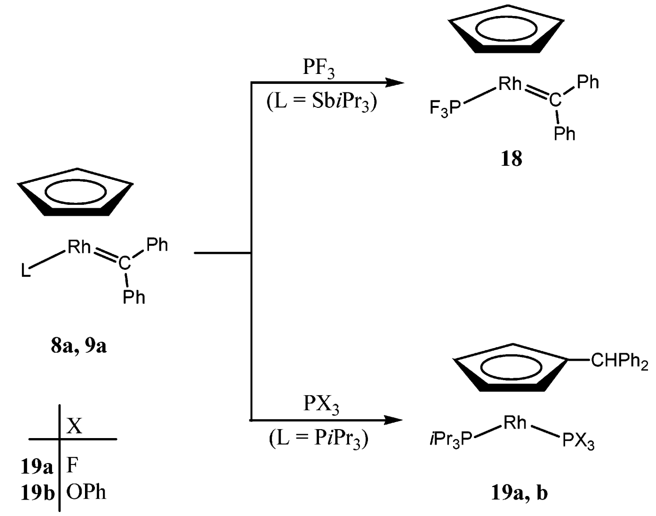
17

π-acceptor properties and are thus able to stabilize molecular fragments such as $[(\eta^5\text{-}C_5H_5)Rh]$, $[(\eta^5\text{-}C_5R_5)Co]$, $[Ni(PR_3)_2]$, etc.[22]

Like the rhodium vinylidenes $[(\eta^5\text{-}C_5H_5)Rh({=}C{=}CHR)(P\mathit{i}Pr_3)]$, the carbene complexes **9h** and **10** also react with sulfur and selenium by addition of the chalcogen to the metal−carbon double bond. By this route, the novel half-sandwiches **16a**−**d** with thio- or selenobenzophenone as ligands were obtained in good to excellent yields (Scheme 7).[15] The X-ray crystal structure analysis of **16b** confirmed the linkage of selenobenzophenone through selenium and carbon to the rhodium center. In comparison with $Se(CH_3)_2$ on one hand and $Se{=}CHCH_3$ on the other, the Se−C distance in **16b** corresponds more to that of a carbon−selenium single bond, which is in agreement with the selenometallacyclopropane structure. The Rh−Se, Rh−C, and C−Se bond lengths as well as the corresponding Rh−Se−C, Rh−C−Se, and C−Rh−Se bond angles of **16b** are quite similar to those in the selenoaldehyde complex $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}SeCHCH_3)(P\mathit{i}Pr_3)]$, which was prepared from $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}SeC{=}CH_2)(P\mathit{i}Pr_3)]$ by catalytic hydrogenation.[23]

Not only sulfur and selenium but also CuCl reacts with the carbonyl derivative **10** by electrophilic addition to the $Rh{=}CPh_2$ bond. Treatment of **10** with 2 equiv of CuCl led to the formation of a deep red, air-stable solid that according to the elemental analysis and the mass spectrum proved to be a 1:2 adduct of **10** and CuCl.[15] The chemical shift of the signal for the $\mathit{C}Ph_2$ carbon atom indicates that the carbene ligand occupies a bridging position, and thus a structure including a four-membered Rh−C−Cu−Cu ring seems possible. The reaction of the 1:2 adduct with an excess of NaC_5H_5 gives the heterobimetallic complex **17** (see Scheme 7), in which the carbene unit bridges two different 16-electron fragments. Compound **17** is a near-relative of the vinylidene-bridged complex $[(\eta^5\text{-}C_5H_5)(P\mathit{i}Pr_3)Rh(\mu\text{-}C{=}CH_2)Cu(\eta^5\text{-}C_5H_5)]$, previously prepared from $[(\eta^5\text{-}C_5H_5)(P\mathit{i}Pr_3)Rh(\mu\text{-}C{=}CH_2)CuCl]$ and NaC_5H_5.[11c]

Scheme 8



18

8a, 9a

	X
19a	F
19b	OPh

19a, b

An Unusual Type of Migratory Insertion Reaction

Following the work on the reactivity of the half-sandwich-type rhodium carbenes toward CO and taking the similar σ-donor/π-acceptor capabilities of CO and PF_3 into account, we also reacted the starting materials **8a** and **9a** with PF_3. These experiments were in particular stimulated by the fact that, although a great number of phosphorus ylides $R_3PCR'_2$ with $R' =$ aryl have been described,[24] to the best of our knowledge the corresponding trifluoro derivative $F_3PCR'_2$ is unknown.

The results of the experiments are outlined in Scheme 8. In analogy to the reaction with CO (see Scheme 4), the stibine complex **8a** reacts with PF_3 by displacement of $Sb\mathit{i}Pr_3$ and formation of the related half-sandwich **18** (Scheme 8). In contrast, treatment of **9a** with PF_3 leads to a migratory insertion of the CPh_2 unit into one of the cyclopentadienyl C−H bonds to afford the ring-substituted product **19a**.[25] Although the phosphite $P(OPh)_3$ is less reactive than PF_3, the reaction of **9a** with an excess of $P(OPh)_3$ proceeds similarly and gives compound **19b**. Regrettably, in neither case could the formation of F_3PCPh_2 be detected. Regarding the molecular structures of both **19a** and **19b**, crystallographic studies revealed that the metal center possesses a somewhat distorted trigonal coordination sphere if the midpoint of the substituted cyclopentadienyl ring is taken as one coordination site. The $Rh{-}PF_3$ as well as the $Rh{-}P(OPh)_3$ bonds are significantly shorter than the $Rh{-}P\mathit{i}Pr_3$ distance, which reflects the distinct difference in the π-acceptor strengths of PF_3 and $P(OPh)_3$ on one hand and $P\mathit{i}Pr_3$ on the other. The $CHPh_2$ group in **19a**,**b** points away from the bulky triisopropylphosphine ligand, which probably reduces the steric repulsion between the two moieties.

The half-sandwich-type carbenes **9a**,**c** also react with Brønsted acids HX by migratory insertion of the CPh_2 unit into one of the C−H bonds of the five-membered ring (Scheme 9). Treatment of the starting materials

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(21) (a) Otsuka, S.; Nakamura, A. *Inorg. Chem.* **1968**, *7*, 2542−2544. (b) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *Organometallics* **1982**, *1*, 732−739. (c) Hörlin, G. Ph.D. Thesis, Universität Würzburg, 1993.

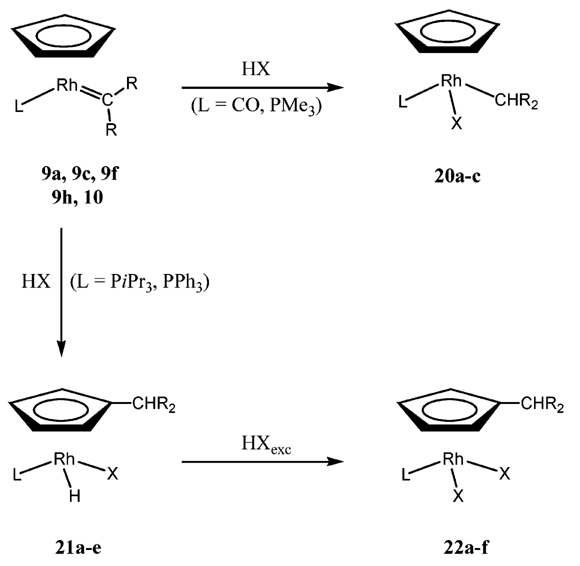
(22) Moore, D. S.; Robinson, S. D. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 1−68.

(23) Werner, H.; Paul, W.; Knaup, W.; Wolf, J.; Müller, G.; Riede, J. *J. Organomet. Chem.* **1988**, *358*, 95−121.

(24) (a) Kosolapoff, G. M.; Maier, L. *Organophosphorus Compounds;* Wiley-Interscience: New York, 1972; Vol. 3. (b) Schmidbaur, H. *Adv. Organomet. Chem.* **1976**, *14*, 205−243.

(25) Herber, U.; Guerrero Sanchez, R.; Gevert, O.; Laubender, M.; Werner, H. *New J. Chem.* **2001**, *25*, 396−399.

Scheme 9



	L	R	X
20a	CO	Ph	Cl
20b	PMe_3	Ph	Cl
20c	PMe_3	Ph	O_2CCF_3
21a, 22a	P*i*Pr_3	Ph	Cl
21b,22b	P*i*Pr_3	Ph	Br

	L/PX_3	R	X
21c, 22c	P*i*Pr_3	Ph	I
21d, 22d	P*i*Pr_3	Ph	O_2CCF_3
21e, 22e	P*i*Pr_3	*p*-Tol	Cl
22f	PPh_3	Ph	Cl

with an equimolar amount of HX (X = Cl, Br, I, CF_3CO_2) in acetone or benzene at room temperature gives the rhodium(III) hydrido complexes **21a**–**e** in excellent yields.[26] For the preparation of **21a**,**b**,**e**, instead of HCl or HBr also Me_3SiCl or Me_3SiBr can be used as the substrate, which in the presence of traces of water generate in situ the corresponding acid HX.

The reactions of **21a**–**e** with a second equivalent of HX afford the dihalo or bis(trifluoroacetato) derivatives **22a**–**e**, which are significantly more stable than the halo hydrido or trifluoroacetato hydrido precursors. In contrast to the PPh_3-containing chloro hydrido compound [{η^5-$C_5H_4(CHPh_2)$}RhH(Cl)(PPh_3)], which is exceedingly labile and could only be characterized by spectroscopic techniques, the corresponding dichloro complex **22f** is quite stable and accessible from **9f** and an excess of HCl in nearly quantitative yield.[26] We note, however, that as part of our studies on the chemistry of half-sandwiches with (η^5-$C_5H_4SiMe_3$)Rh as a building block, we were able to isolate the rhodium(III) chloro hydrido compound [{η^5-$C_5H_3(CHPh_2)SiMe_3$}RhH(Cl)(PPh_3)], which is considerably more stable than the {η^5-$C_5H_4(CHPh_2)$}Rh counterpart.[18]

By using a labeling experiment, we shed light on the mechanism of formation of the ring-substituted complexes **21a**–**e**.[26] Treatment of **9a**-d_5, which was prepared from *trans*-[RhCl(=CPh_2)(P*i*Pr_3)$_2$] and TlC_5D_5 in THF, with an equimolar amount of HCl in benzene led exclusively to the formation of the chloro deuterio compound **21a**-d_5 (Scheme 10). Regarding the individual steps of this reaction, we assume that initially an addition of HCl to the carbene–rhodium bond takes place to give the intermediate **A**, which is structurally related to **20a**,**b**. Migration of the $CHPh_2$ unit to the C_5D_5 ligand generates the substituted cyclopentadienerhodium(I) species **B**, which, following a 1,2-D shift along the five-membered ring, would afford intermediate **C**. The final product **21a**-d_5 is subsequently obtained by deuterium transfer from the sp^3 carbon atom of the diene to the metal center. The reaction of **21a**-d_5 with HCl gives the tetradeuterio derivative **22a**-d_4. With respect to intermediate **C**, there is some evidence that an isotopomer of the composition [RhCl(η^4-$C_5H_5CHPh_2$)(P*i*Pr_3)] is involved in the reaction of the dimer **23** with $C_5H_5CHPh_2$ to form **21a** (see Scheme 10). This method to prepare **21a** is reminiscent of earlier work from our laboratory illustrating that treatment of **23** with cyclopentadiene affords the rhodium(III) complex [(η^5-C_5H_5)RhH(Cl)(P*i*Pr_3)] in nearly quantitative yield.[27] The molecular structure of **22a** has been determined crystallographically.[26]

The results of some complementary studies concerning the reactivity of the rhodium carbenes **8a** and **9a** toward electrophiles are summarized in Scheme 11. As shown by the proposed molecular structures, both HBF_4 and Meerwein's reagent [OMe_3]BF_4 as well as methyl triflate behave similarly toward the half-sandwich-type rhodium carbenes and afford the η^3-benzyl complexes **24** and **25a**–**c** in 82–97% yield.[26] The comparison of the ^1H and ^{13}C NMR data with those of the related ruthenium complexes **51** and **52** (see Scheme 19) strongly suggest that in all cases the exo isomer with the plane of the η^3-benzylic unit pointing away from rhodium is preferred. Moreover, in solution the structures are rigid, which means that the η^3-bonded fragment does not rotate around the metal–ligand axis on the NMR time scale.

The pathway to convert rhodium(I) η^5-indenyl carbenes [(η^5-C_9H_7)Rh(=CPh_2)(L)] into ring-substituted derivatives by migratory insertion of the CPh_2 moiety into one of the C–H bonds of the five-membered ring is somewhat distinct from that found for the (η^5-C_5H_5)Rh counterparts. While the η^5-cyclopentadienyl complexes [(η^5-C_5H_5)Rh(=CPh_2)(L)] (**8a**, **9a**) react with CO by substitution either of L or of the carbene, thereby leaving the ring ligand unchanged (see Scheme 4), treatment of the η^5-indenyl compounds **26a**–**e** with carbon monoxide leads to the exclusive formation of the ring-substituted complexes **27a**–**e** (Scheme 12).[28] Since no byproducts are formed, we assume that the course of the reaction of **26a**–**e** with CO is similar to that of the reaction of **9a** with PF_3 and $P(OPh)_3$. In agreement with the kinetic studies mentioned above,[20] it is conceivable that the initial step consists of a bimolecular process leading to a short-lived 1:1 adduct of the starting materials **26a**–**e** and CO. This 20-electron intermediate could generate via a ring slippage the stereochemical isomer [(η^3-C_9H_7)Rh(=CPh_2)(CO)(L)] with a η^3-bonded indenyl ligand and an 18-electron configuration at rhodium, which then rearranges to the isolated product. In this context it is interesting to note that the X-ray crystal structure analyses of both **26a** and **27b** revealed that in either case there is a moderate slip distortion from a η^5 to a η^3 coordination mode of the indenyl unit,

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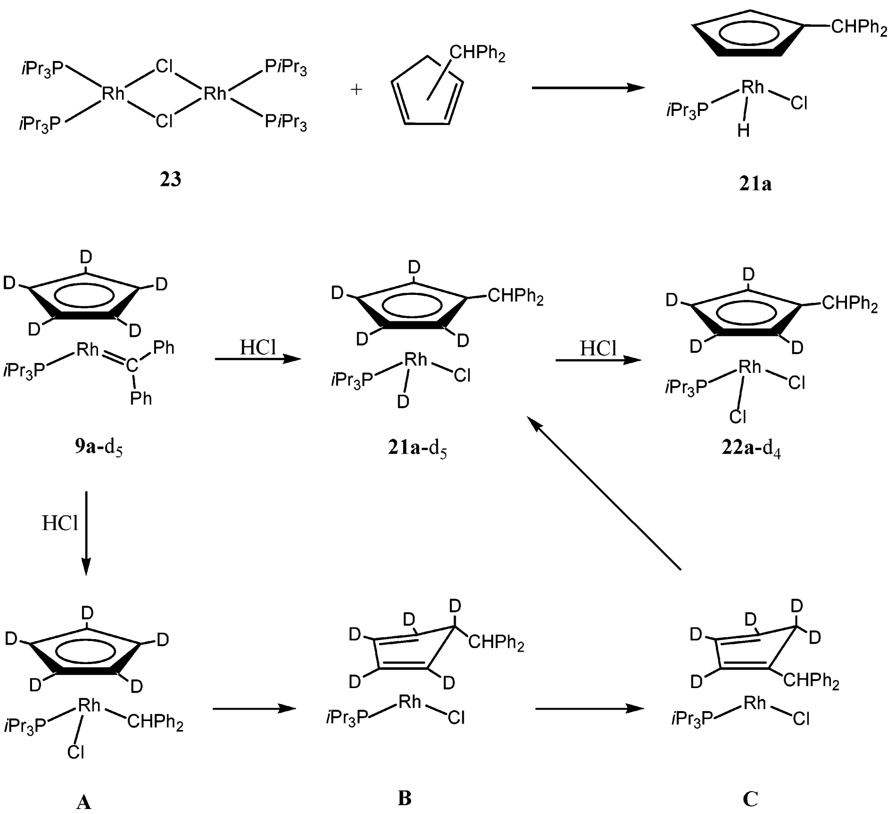
(26) Bleuel, E.; Schwab, P.; Laubender, M.; Werner, H. *Dalton* **2001**, 266–273.

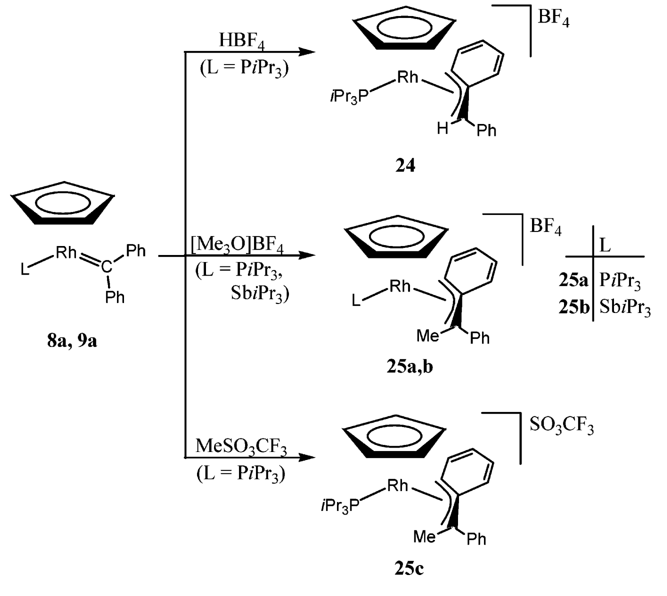
(27) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395–407.

(28) Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 3109–3114.

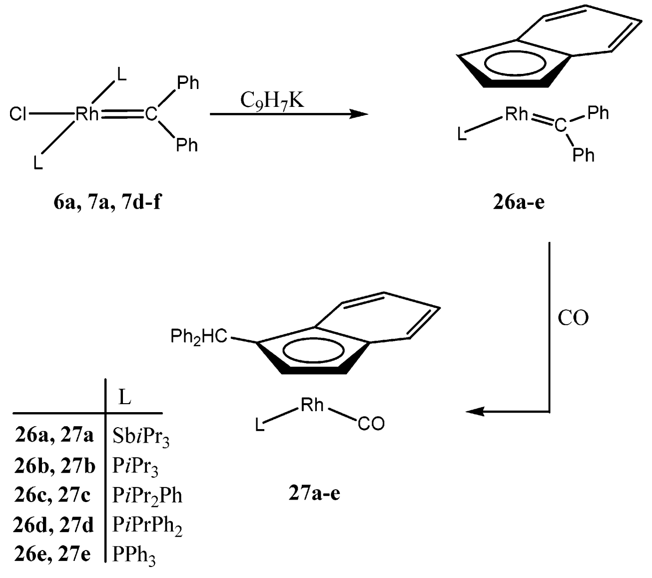
Scheme 10



Scheme 11



Scheme 12



being obviously independent of the presence of the bulky $CHPh_2$ group.

By doing a quick sidestep from rhodium to iridium, we found that also with this metal the conversion of $(\eta^5\text{-}C_5H_5)M(=CPh_2)$ to an isomeric $\{(\eta^5\text{-}C_5H_4(CHPh_2)\}M$ fragment could be achieved. The four-coordinate carbene complex **28**, being easily accessible from $[IrCl(C_2H_4)(Sb\textit{i}Pr_3)(P\textit{i}Pr_3)]$ and diphenyldiazomethane, reacts with NaC_5H_5 to give the required half-sandwich **29** by elimination of the more weakly bound triisopropylstibine ligand (Scheme 13). In contrast to the labile methylene compound $[(\eta^5\text{-}C_5Me_5)Ir(=CH_2)(PMe_3)]$, generated upon photolysis of the metallacycle $[(\eta^5\text{-}C_5Me_5)Ir(\kappa^2\text{-}C,O\text{-}CH_2CMe_2O)(PMe_3)]$ at −60 °C,[30] the diphenylcarbene complex is thermally quite stable and decomposes only at temperatures above 93 °C. Compound **29** possesses the expected two-legged piano-stool configuration with an $Ir{-}CPh_2$ bond length that is nearly identical with that of the related half-sandwich-type rhodium carbene **10**.[29]

The protonation of **29** with HCl occurs stepwise and affords the alkyliridium(III) complex **30** in virtually quantitative yield. While the analogous rhodium species is highly labile, **30** is completely stable at room tem-

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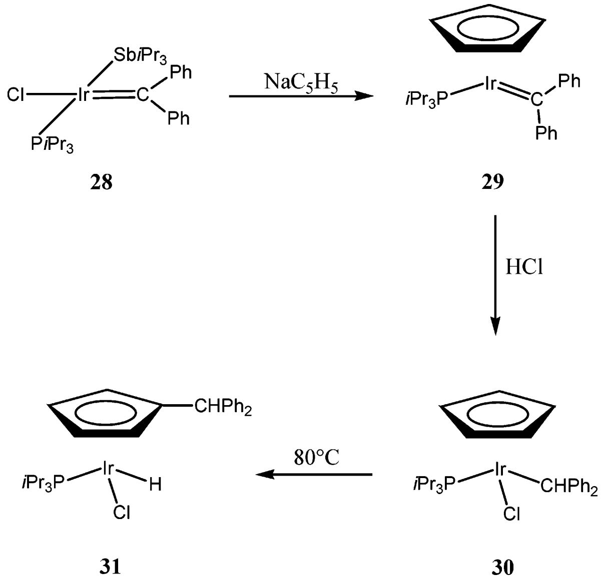
(29) Ortmann, D. A.; Weberndörfer, B.; Ilg, K.; Laubender, M.; Werner, H. *Organometallics* **2002**, *21*, 2369−2381.

Scheme 13

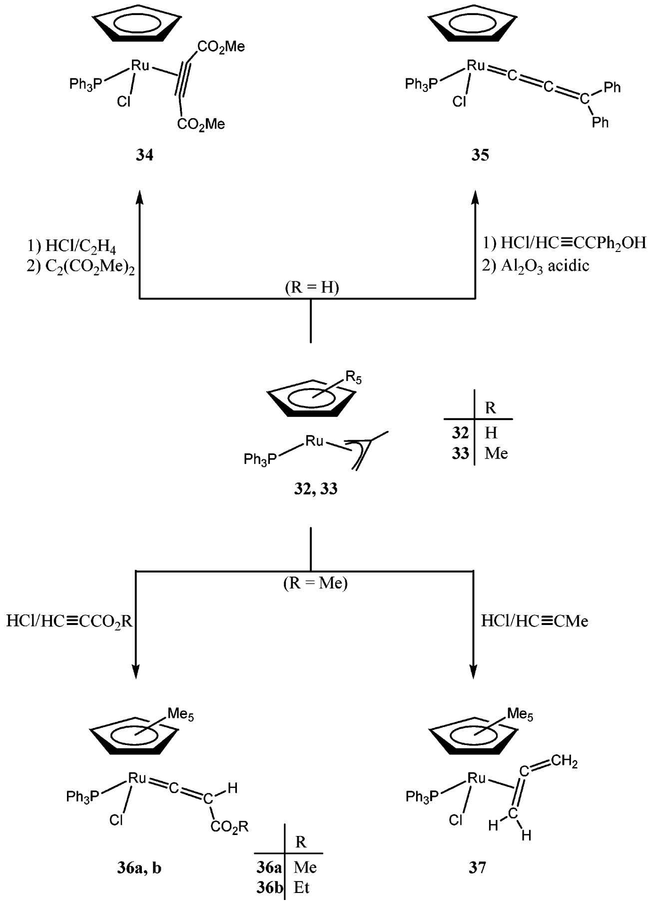


perature and in the absence of air can be stored for weeks without decomposition. However, stirring a solution of **30** in benzene for 2 min at reflux leads to the formation of the chloro hydrido compound **31**, containing a substituted ring ligand. Since during the rearrangement the color of the solution changes first from orange-yellow to red and after some seconds from red to yellow, we assume that initially the four-coordinate cyclopentadieneiridium(I) derivative [IrCl(η^4-$C_5H_5CHPh_2$)(P*i*Pr$_3$)] (comparable to intermediate **B** or **C** in Scheme 10) is formed. It subsequently reacts by hydrogen transfer from carbon to the metal to give the iridium(III) isomer. The reaction of **29** with HBF_4 gives a cationic η^3-benzyliridium complex, the structure of which probably is analogous to that of the rhodium counterpart **24** (see Scheme 11).[29]

A Valuable Preparative Tool: Half-Sandwich-Type Ruthenium Carbenes

At about the same time when we entered the field of ruthenium η^5-cyclopentadienyl complexes with a 16-electron count,[31,32] we also discovered the versatility of the η^3-allyl compounds **32** and **33** as starting materials for the preparation of ruthenium half-sandwiches containing Ru=C double bonds. When we started this work, we were particularly interested to find out whether complexes of the general composition [(η^5-C_5R_5)RuX(=CRR′)(L)] and [(η^5-C_9H_7)RuX(=CRR′)(L)] would behave similarly to the Grubbs-type ruthenium carbenes [$RuCl_2$(=CHR)(PR′$_3$)$_2$],[33] which nowadays belong to the most frequently used organometallic compounds, in both organic synthesis and homogeneous catalysis.

Scheme 14



The first results of our studies concerning this subject are outlined in Scheme 14.[34] The η^5-cyclopentadienyl complex **32** reacts with HCl in the presence of ethene to give the intermediate [(η^5-C_5H_5)RuCl(C_2H_4)(PPh_3)], which upon treatment with $C_2(CO_2Me)_2$ readily undergoes ligand exchange to give the alkyne derivative **34**. If under similar conditions, without the ethene atmosphere, compound **32** is treated with the substituted propargylic alcohol HC≡CCPh_2OH, the vinylidene complex [(η^5-C_5H_5)RuCl{=C=CHC(OH)Ph_2}(PPh_3)] is generated initially, which subsequently reacts with acidic Al_2O_3 by elimination of water to give the allenylidene compound **35**.[35]

The reactions of **33** with HCl and methyl or ethyl propiolate afford the ruthenium vinylidenes **36a**,**b**, of which **36a** was independently prepared by Bruce et al. using [(η^5-C_5Me_5)RuCl(PPh_3)$_2$] as the precursor.[36] In contrast to HC≡CCO_2Me, propyne reacts with **33** in the presence of HCl to form the allene complex **37**, which is fluxional in solution. On the basis of VT NMR measurements in the temperature range 293−343 K,

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(30) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079−3080.

(31) Braun, T.; Laubender, M.; Gevert, O.; Werner, H. *Chem. Ber./Recl.* **1997**, 130, 559−563.

(32) For related work on 16-electron complexes [(η^5-C_5R_5)RuX(L)], see: (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278−280. (b) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308−1314. (c) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1990**, *9*, 1106−1112. (d) Luo, L.; Nolan, S. *Organometallics* **1994**, *13*, 4781−4786. (e) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488−499.

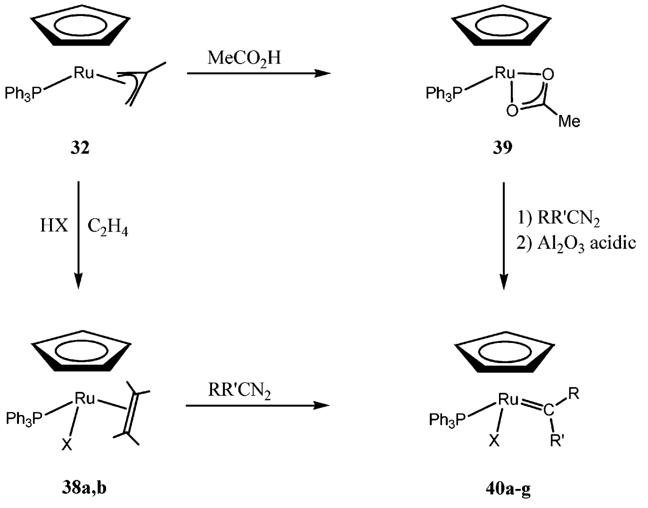
(33) (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (b) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857. (c) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (d) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110. (e) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450.

(34) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291−7292.

(35) Braun, T.; Münch, G.; Windmüller, B.; Gevert, O.; Laubender, M.; Werner, H. *Chem. Eur. J.* **2003**, *9*, 2516−2530.

(36) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *522*, 307−310.

Scheme 15



	R
38a	Cl
38b	CF_3CO_2

X = Cl	R/R'
40a	$(Ph)_2$
40b	(Ph)/(*p*-Tol)
40c	$(p\text{-}C_6H_4Cl)_2$
40d	$(p\text{-}C_6H_4OMe)_2$

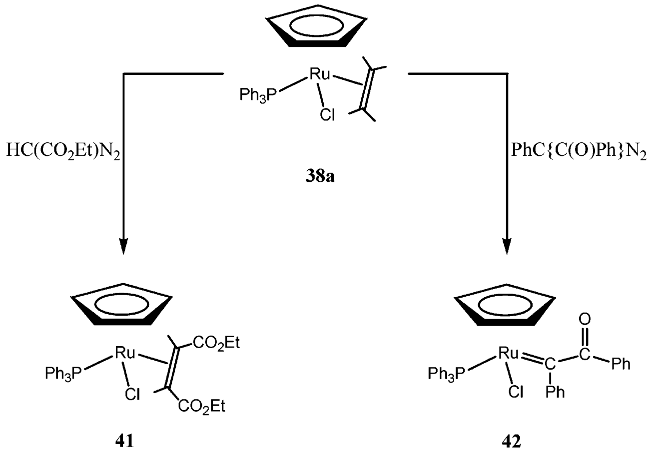
X = CF_3CO_2	R/R'
40e	$(Ph)_2$
40f	$(p\text{-}C_6H_4Cl)_2$
40g	$(p\text{-}C_6H_4OMe)_2$

we assume that two distinct dynamic processes take place. One could be a rotation of the allene ligand about the metal–allene axis, while the second probably is a migration of the metal from one C=C bond to the next. To explain the course of the isomerization of propyne to allene in the coordination sphere of ruthenium, it is conceivable that in the initial step the expected alkyne compound $[(\eta^5\text{-}C_5Me_5)RuCl(CH_3C{\equiv}CH)(PPh_3)]$ is formed. This could generate, after protonation and hydride shift from ruthenium to the CH carbon of the alkyne, the cationic vinyl derivative $[(\eta^5\text{-}C_5Me_5)RuCl\{C(CH_3){=}CH_2\}(PPh_3)]^+$, which rearranges to the allene hydrido isomer $[(\eta^5\text{-}C_5Me_5)RuH(Cl)(\eta^2\text{-}CH_2{=}C{=}CH_2)(PPh_3)]^+$ and finally affords the product **37** by deprotonation.[35] Precedence for the metal-assisted conversion of alkynes (not only propyne) to allenes stems from previous studies both by Richards et al. on six-coordinate rhenium(I) compounds[37] and by us on square-planar as well as half-sandwich-type rhodium(I) and iridium(I) complexes.[38]

The required half-sandwich-type ruthenium carbenes $[(\eta^5\text{-}C_5H_5)RuX({=}CRR')(PPh_3)]$ are accessible by two routes (see Scheme 15). In our initial work,[34] the acetato derivative **39** was used as the starting material, which reacts with diaryldiazomethanes with partial opening of the chelate ring to give the intermediates $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}O_2CCH_3)({=}CRR')(PPh_3)]$. These were converted to the analogous carbene chloro compounds **40a–d** with $[HNEt_3]Cl$ or, more conveniently, with Al_2O_3 in the presence of chloride.[34,39]

The alternative route proceeds via the in situ generated ethene complexes **38a**,**b**, which react with $RR'CN_2$ in toluene at room temperature to give the ruthenium carbenes **40a**,**e–g** in 60–80% yield.[35] The chloro derivative **40a** also has been prepared by Baratta et al. from $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ and an excess of diphenyldiazomethane as the precursors.[40] The X-ray crystal structure analysis of **40a** revealed[39] that the molecule has a three-legged piano-stool configuration with a $Ru{-}CPh_2$ bond distance of 1.92(2) Å, which is nearly the same as in the Fischer-type carbene complex $[(\eta^5\text{-}C_5H_5)RuI\{{=}C(OEt)Ph\}(CO)]$.[41]

Scheme 16



In contrast to the reaction with diaryldiazomethanes, the ruthenium ethene derivative **38a** reacts with 2 equiv of ethyl diazoacetate to afford exclusively the diethyl maleate complex **41** (Scheme 16). The expected carbene compound $[(\eta^5\text{-}C_5H_5)RuCl({=}CHCO_2Et)(PPh_3)]$ possibly is formed as an intermediate, since this species has been detected upon treatment of a solution of $[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}O_2CCH_3)(PPh_3)]$ with $HC(CO_2Et)N_2$ and Me_2SiCl_2 at low temperature.[42] A ruthenium carbene with a $Ru{=}CHCO_2Et$ linkage probably also is involved in the stereoselective conversion of ethyl diazoacetate to diethyl maleate catalyzed by various ruthenium half-sandwiches $[(\eta^5\text{-}C_5R_5)RuX(PR'_3)_2]$.[42]

The olefin precursor **38a** reacts also with the diazo ketone $PhC\{C(O)Ph\}N_2$ (azibenzil) to give the air-stable carbene complex **42**, the molecular structure of which has been determined crystallographically.[35] The spectroscopic data of **42** are interesting insofar as at low temperature in the ^{13}C NMR spectrum two signals due to the cyclopentadienyl carbon atoms and in the ^{31}P NMR spectrum two resonances due to the phosphorus atom of the PPh_3 ligand appear. On the basis of VT ^{31}P NMR measurements, the free enthalpy of activation at coalescence (293 K at 162.0 Hz) is ca. 38 kJ/mol. A tentative explanation is that in solution two rotamers of **42** exist, which differ in the orientation of the two substituents Ph and C(O)Ph around the Ru–C(carbene) axis. A hindered rotation around a Ru=C axis is not unique and has already been observed by Studabaker and Brookhart in the case of the cationic methylene complex $[(\eta^5\text{-}C_5H_5)Ru({=}CH_2)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)]AsF_6$.[43]

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(37) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc.*, *Chem. Commun.* **1984**, 992–993.

(38) (a) Werner, H.; Höhn, A. *J. Organomet. Chem.* **1984**, *272*, 105–113. (b) Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164–1169. (c) Werner, H.; Schwab, P.; Mahr, N.; Wolf, J. *Chem. Ber.* **1992**, *125*, 2641–2650.

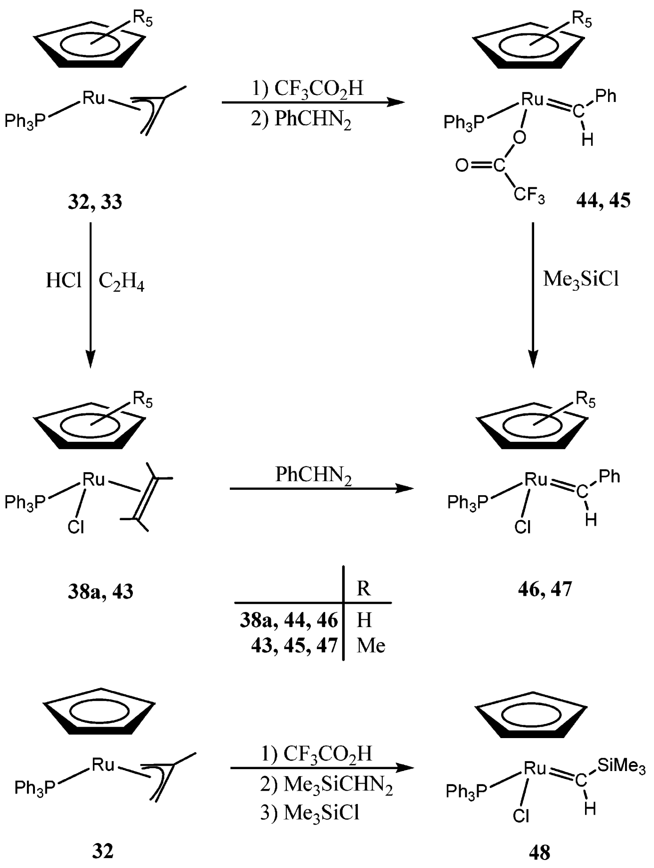
(39) Werner, H.; Braun, T.; Daniel, T.; Gevert, O.; Schulz, M. *J. Organomet. Chem.* **1997**, *541*, 127–141.

(40) Baratta, W.; Herrmann, W. A.; Kratzer, R. M.; Rigo, P. *Organometallics* **2000**, *19*, 3664–3669.

(41) Adams, H.; Bailey, N. A.; Ridgway, C.; Taylor, B. F.; Walters, S. J.; Winter, M. J. *J. Organomet. Chem.* **1990**, *394*, 349–364.

(42) Baratta, W.; Del Zotto, A.; Rigo, P. *Organometallics* **1999**, *18*, 5091–5096.

Scheme 17

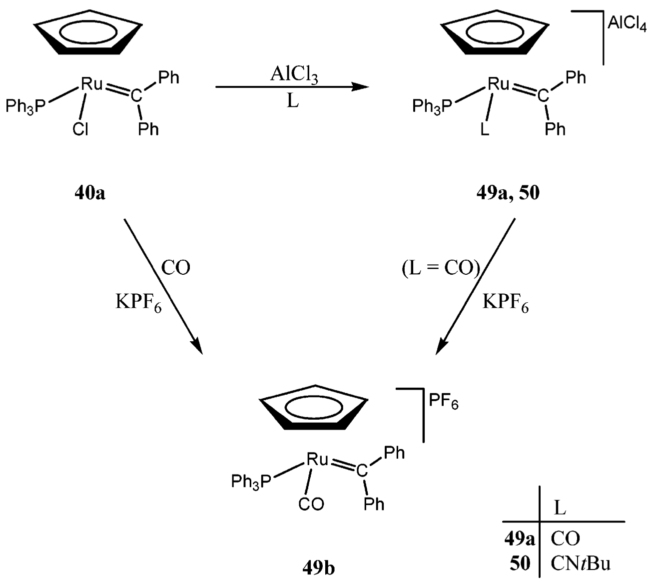


	R
38a, 44, 46	H
43, 45, 47	Me

In contrast to rhodium, where half-sandwiches $[(\eta^5\text{-}C_5H_5)Rh(=CR_2)(PR'_3)]$ could hitherto only be prepared with R = aryl, related ruthenium compounds are also accessible with CHPh and $CHSiMe_3$ as carbene ligands.[35] The synthetic routes are summarized in Scheme 17. Stepwise treatment of **32** or **33** first with CF_3CO_2H and then with $PhCHN_2$ gives the carbene(carboxylato) derivatives **44** and **45**, which are converted with Me_3SiCl to the corresponding carbene chloro complexes **46** and **47**. These have also been prepared by substitution of the olefinic ligand in the ethene chloro compounds **38a** and **43** by phenyldiazomethane. The analogous (trimethylsilyl)carbene complex **48** was obtained in a one-pot reaction from **32**, CF_3CO_2H, Me_3SiCHN_2, and Me_3SiCl, probably via $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}O_2CCF_3)(=CHSiMe_3)(PPh_3)]$ as an intermediate. Quite recently, the Grubbs group reported the preparation of a relative of **44** with tris(pyrazolyl)borate instead of cyclopentadienyl and diphenylmethyl acetate instead of trifluoroacetate as ligands,[44] but neither this compound nor the half-sandwiches **44**−**48** proved to be useful catalysts in olefin metathesis.

The conversion of the neutral compound **40a** to the cationic carbene carbonyl and carbene isocyanide complexes **49a**,**b** and **50** could be achieved by using either $AlCl_3$ or KPF_6 as the substrate to cleave the Ru−Cl bond (see Scheme 18). As the X-ray crystal structure analysis of **49b** confirmed, the Ru−CPh_2 bond length is somewhat longer than that in the precursor **40a**, indicating that due to the positive charge at ruthenium the metal-to-ligand back-bonding is weakened. The distance Ru−CO is about 0.11 Å shorter than the distance Ru−CPh_2, which is in agreement with the stronger π-acceptor capability of CO compared with that of diphenylcarbene.[35]

Scheme 18



	L
49a	CO
50	CN*t*Bu

While in metal carbenes of the Schrock type, containing an electron-poor transition-metal center, the $M{=}CR_2$ bond is preferentially attacked by electrophiles,[45] the ruthenium carbenes of the general composition $[(\eta^5\text{-}C_5H_5)RuCl(=CR_2)(PPh_3)]$ are highly reactive toward nucleophiles. Treatment of **40a** with either $LiHBEt_3$ or PhLi leads to a conversion of the CPh_2 to a benzylic unit, which on the basis of the NMR data is η^3-bonded to the metal. In analogy to the rhodium complexes **24** and **25a**−**c** (see Scheme 11), we suppose that in the related ruthenium compounds **51** and **52** the benzylic ligand also has an exo and not an endo configuration with respect to the $(\eta^5\text{-}C_5H_5)Ru(PPh_3)$ fragment (Scheme 19). Regarding the mechanism of formation of **51**, we assume that the carbene hydrido compound $[(\eta^5\text{-}C_5H_5)RuH(=CPh_2)(PPh_3)]$ is formed as an intermediate which, after insertion of the carbene unit into the Ru−H bond, generates a Ru−$CHPh_2$ species. Subsequent rearrangement of the diphenylmethyl moiety from η^1 to η^3 would yield the product.[35]

The reactions of **40a**,**c**,**d** with vinyl Grignard reagents led to the displacement of the chloro ligand and formation of the 1,1-diarylallyl complexes **53**−**55**. The ^1H, ^{13}C, and ^{31}P NMR spectra of these complexes illustrate quite clearly that in each case a mixture of the exo (a) and endo (b) isomers is formed, the ratio being approximately 2:1. Attempts to separate the isomeric mixture of **53a** and **53b** by low-temperature chromatography and fractional crystallization resulted in the isolation of single crystals, which were composed exclusively of the exo isomer **53a**. As the X-ray crystal structure analysis revealed, the bond lengths between the metal and the terminal carbon atoms of the allylic unit in **53a** are unequal and differ by 0.06 Å. This is in contrast to

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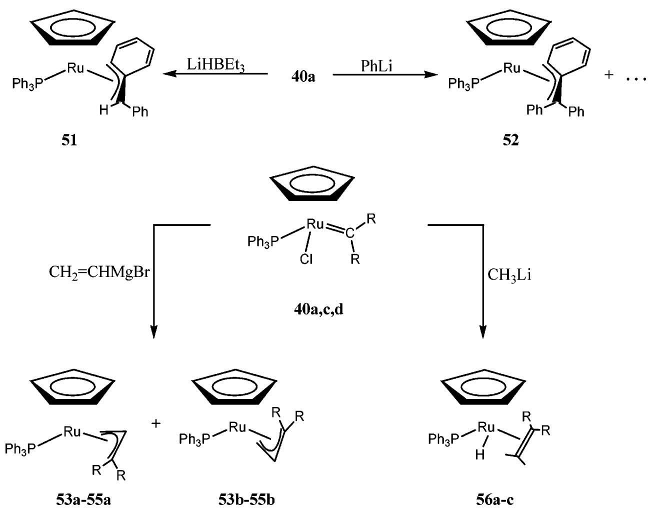
(43) Studabaker, W. B.; Brookhart, M. *J. Organomet. Chem.* **1986**, *310*, C39−C41.

(44) Sanford, M. S.; Valdez, M. R.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5455−5463.

(45) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98−104.

Scheme 19



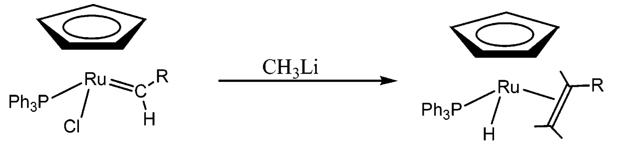
	R
53, 56a	C_6H_5
54, 56b	*p*-C_6H_4Cl
55, 56c	*p*-C_6H_4OMe

the situation found for [(η^5-C_5H_5)Ru(η^3-2-MeC_3H_4)(PPh_3)][46] and [(η^5-C_5H_5)Ru(η^3-2-MeC_3H_4)(CO)],[47] which have both been prepared from appropriate (η^5-C_5H_5)Ru precursors and allyl Grignard reagents. To explain the formation of **53**–**55**, we assume that from **40a**,**c**,**d** and CH_2=CHMgBr a metal carbene η^1-vinyl derivative is generated initially which, by intramolecular C–C coupling, rearranges to afford the products. In this context, we note that Hill and co-workers recently showed that a carbene and a vinyl unit can be coupled to an allyl ligand also on the reverse route by treating the five-coordinate vinylruthenium(II) compound [RuCl(CH=CH_2)(CO)(PPh_3)$_2$] with diazomethane as a carbene source.[48]

The carbene complexes **40a**,**c**,**d** also react with methyllithium in diethyl ether to give, after addition of acetone, brownish reaction mixtures from which the olefin hydrido compounds **56a**–**c** have been isolated in good yields.[35] From a mechanistic point of view it seems conceivable that the initial product in these reactions is the corresponding carbene methyl derivative [(η^5-C_5H_5)$RuCH_3$(=CR_2)(PPh_3)], which by migratory insertion generates the 16-electron alkylruthenium(II) intermediate [(η^5-C_5H_5)Ru(η^1-CR_2CH_3)(PPh_3)], which subsequently rearranges by a β-H shift to give the olefin hydrido compounds **56a**–**c**. A similar mechanism probably operates in the formation of the complexes **57** and **58** (Scheme 20), which were obtained by reaction of **46** and **48** with MeLi as moderately air-sensitive solids in 60–70% yield.[35]

Cleavage of the η^3-benzyl– and η^3-allyl–ruthenium bonds in **51** and **53a**,**b**–**55a**,**b** by acetic acid in benzene proceeds slowly and affords diphenylmethane and the olefins R_2C=$CHCH_3$, respectively. The organometallic product is the acetatoruthenium(II) compound **39**, which can be easily converted to the carbene complexes

Scheme 20



46, 48

57, 58

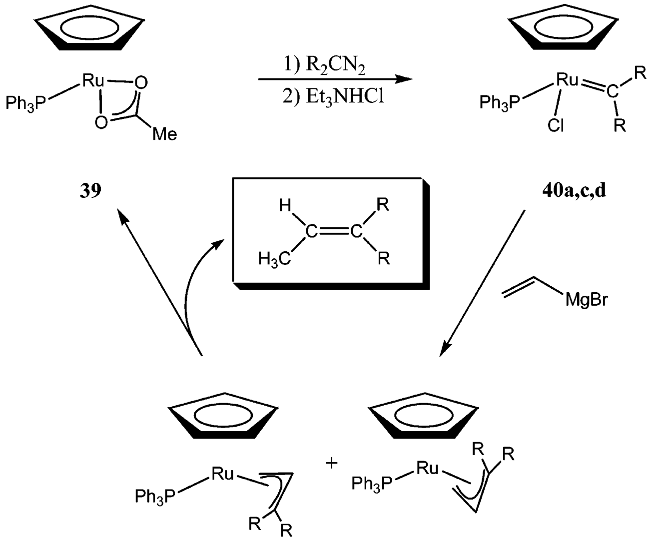
	R
57	Ph
58	$SiMe_3$

Scheme 21

51 + CH_3CO_2H $\longrightarrow$ Ph_2CH_2 + **39**

53a,b-55a,b + CH_3CO_2H $\longrightarrow$ R_2C=$CHCH_3$ + **39**

Scheme 22



53a-55a **53b-55b**

40a,**c**,**d** (see Scheme 15). Thus, it is possible to develop a cyclic process in which the trisubstituted ethene derivatives can be built up from a carbene ligand (generated from a diazoalkane), a vinyl unit, and a proton in the coordination sphere of ruthenium(II) (Scheme 22).[35] Most recently, we also reported a protocol for the preparation of a series of ruthenium half-sandwiches [(η^5-C_9H_7)RuX(=CRR′)(PPh_3)] with CPh_2, CHPh, and $CHSiMe_3$ as carbene ligands, which similarly to the cyclopentadienyl analogues are potentially useful starting materials for making C–C bonds with the CRR′ moiety as one building block and organolithium or Grignard compounds as coupling reagents.[49]

Last but not Least: Osmium Carbenes with Arenes as Protecting Ligands

After we discovered that osmium(II) vinylidenes [(η^6-arene)OsX(=C=CHR)(L)]PF_6 as well as related allenylidenes [(η^6-arene)OsX(=C=C=CR_2)(L)]PF_6 are accessible from [(η^6-arene)OsX_2(L)] as the precursor,[50,51] we were interested to find out whether related osmium

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[46] Lehmkuhl, H.; Mauermann, M.; Benn, R. *Liebigs Ann. Chem.* **1980**, 754–767.

[47] Hsu, L.-Y.; Nordman, C. E.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1982**, *1*, 134–137.

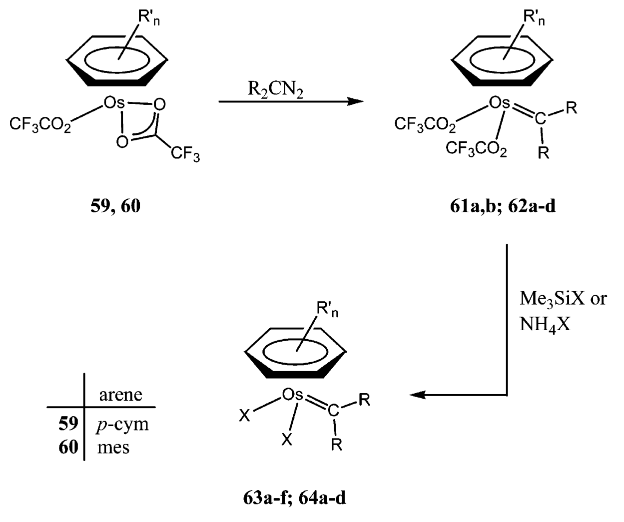
[48] Hill, A. F.; Ho, C. T.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1997**, 2207–2208.

[49] Werner, H.; Münch, G.; Laubender, M. *Inorg. Chim. Acta*, in press.

[50] Knaup, W.; Werner, H. *J. Organomet. Chem.* **1991**, *411*, 471–489.

[51] Weberndörfer, B.; Werner, H. *Dalton* **2002**, 1479–1486.

Scheme 23[a]



59, 60

61a,b; 62a-d

63a-f; 64a-d

	arene
59	*p*-cym
60	mes

	arene	R
61a	*p*-cym	Ph
61b	*p*-cym	*p*-Tol
62a	mes	Ph
62b	mes	*p*-Tol
62c	mes	*p*-C_6H_4Cl
62d	mes	*p*-C_6H_4OMe

	arene	R	X
63a-c	*p*-cym	Ph	Cl/Br/I
63d-f	*p*-cym	*p*-Tol	Cl/Br/I
64a,b	mes	Ph	Cl/I
64c	mes	*p*-Tol	Cl
64d	mes	*p*-C_6H_4OMe	Cl

[a] Legend: L = *p*-cym = 1,4-MeC_6H_4*i*Pr; Mes = 1,3,5-$C_6H_3Me_3$.

carbenes can be prepared by a similar route. However, all attempts to obtain the required compounds [(η^6-arene)OsX(=CRR′)(L)]PF_6 from [(η^6-arene)OsX_2(L)] or [(η^6-arene)OsX(C_2H_4)(L)]PF_6 and RR′CN_2 failed.[52]

The successful methodology to obtain osmium(II) complexes with non-Fischer-type carbenes is outlined in Scheme 23.[53] By taking into consideration that ruthenium half-sandwiches [(η^5-C_5H_5)RuX(=CRR′)-(PPh_3)] had been prepared from [(η^5-C_5H_5)Ru(κ^2-O_2-CMe)(PPh_3)] and diazoalkanes (see Scheme 15), we chose the bis(trifluoroacetates) **59** and **60** as starting materials and treated these with RR′CN_2. From previous work it was known that **60** reacts with CO and various phosphines in benzene at room temperature to give the corresponding 1:1 adducts, thereby converting one of the trifluoroacetato ligands from a κ^2- to a κ^1-bonding mode.[54]

Under similar conditions, the osmium carbenes **61a**,**b** and **62a**−**d** were prepared and isolated as deeply colored, slightly air-sensitive solids in good to excellent yields. Treatment of **61a**,**b** and **62a**−**d** with either Me_3SiX or NH_4X (X = Cl, Br, I) led to a ligand exchange and resulted in the formation of the dichloro, dibromo, and diiodo counterparts **63a**−**f** and **64a**−**d**. Attempts to substitute the CF_3CO_2 units in **61a** or **62a** by fluoride failed, independent of whether NaF, CsF, AgF, or [N*n*Bu_4]F was used as the fluoride source. The reactions of **64a**,**c** with PPh_3 in the presence of $AgPF_6$ afford the cationic complexes [(η^6-mes)OsCl(=CR_2)(PPh_3)]PF_6 (R = Ph, *p*-Tol), which could not be prepared by treatment of [(η^6-mes)$OsCl_2$(PPh_3)] with $AgPF_6$ and diazoalkanes.[53]

The X-ray crystal structure analyses of **62b** and **64a** revealed that in both cases the bond lengths between osmium and the carbon atom of the carbene ligand are nearly the same. Since it is also almost identical with the Os−CRR′ distances in the five-ccordinate osmium(0) compound [OsCl(=CF_2)(NO)(PPh_3)$_2$][55] and the six-coordinate osmium(II) complexes [OsH(Cl)(=CHR)(CO)-(P*i*Pr_3)$_2$] (R = CO_2Et, $SiMe_3$) and [$OsCl_2$(=CHPh)-(CO)(P*i*Pr_3)$_2$],[56] we assume that the strength of the osmium−carbene bond is not significantly influenced by the type of carbene and the coordination number of the metal center. An interesting facet is that single crystals of **64a**, which were grown from CH_2Cl_2/pentane and contain a half-molecule of dichloromethane in the asymmetric unit, built a network between the half-sandwich-type complex and the solvent with H−Cl−H bridges as the decisive element.

The reactions of **62a** and **64a** with C_6H_5MgBr and CH_3MgI led to the substitution of the two chloro or the two trifluoroacetato ligands by bromide or iodide and gave the osmium carbenes **65** and **66** in good yield.[53b] This halide-to-halide exchange with RMgX as the substrate is surprising, insofar as the reactions of [(η^6-mes)$OsCl_2$(CNMe)] with C_6H_5MgBr or CH_3MgI resulted partly or completely in the replacement of chloride by phenyl or methyl, respectively.[57] Even by changing the reaction conditions, we were unable to generate an osmium carbene complex with an Os−C_6H_5 or Os−CH_3 bond using **62a** or **64a** as the precursor.

In contrast to C_6H_5MgBr, the vinyl Grignard reagent CH_2=CHMgBr reacts with the half-sandwich **62a** at low temperature to give the osmium(II) η^3-allyl compound **67**, in which the unsymmetrical η^3-CH_2CHCPh_2 ligand probably is linked in a position exo to the (η^6-mes)OsBr moiety.[53] We assume that in the reaction of **62a** with CH_2=CHMgBr a carbene η^1-vinyl species is generated as an intermediate, which by intramolecular C−C coupling is transformed to the final product. Although an alternative pathway, addition of the C-nucleophile to the carbene carbon atom followed by elimination of trifluoroacetate with concomitant η^1-/η^3-allyl rearrangement, could equally be discussed, we consider this mechanistic route as less likely. In the presence of trifluoracetic acid, the osmium compound **67** behaves similarly to the ruthenium analogues **53**−**55** (see Scheme 21) and affords in addition to [(η^6-mes)OsBr(κ^2-O_2CCF_3)] the trisubstituted olefin Ph_2C=$CHCH_3$.

A C−C coupling reaction involving the CPh_2 ligand also occurs upon treatment of **62a** with ethyl vinyl ether and Na_2CO_3 (Scheme 24). On the basis of the ^1H and ^{13}C NMR spectra of the isolated complex **68** it seems that the anion of a 3,3-diphenylallyl ether is coordinated to the metal via carbon and oxygen in a chelating fashion. To explain the mechanism of formation of **68**, it is conceivable that in the initial step a displacement of one carboxylate ligand by CH_2=CHOEt takes place,

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(52) Henig, G. Ph.D. Thesis, Universität Würzburg, 1997.

(53) (a) Weberndörfer, B.; Henig, G.; Werner, H. *Organometallics* **2000**, *19*, 4687−4689. (b) Weberndörfer, B.; Henig, G.; Hockless, D. C. R.; Bennett, M. A.; Werner, H. *Organometallics* **2003**, *22*, 744−758.

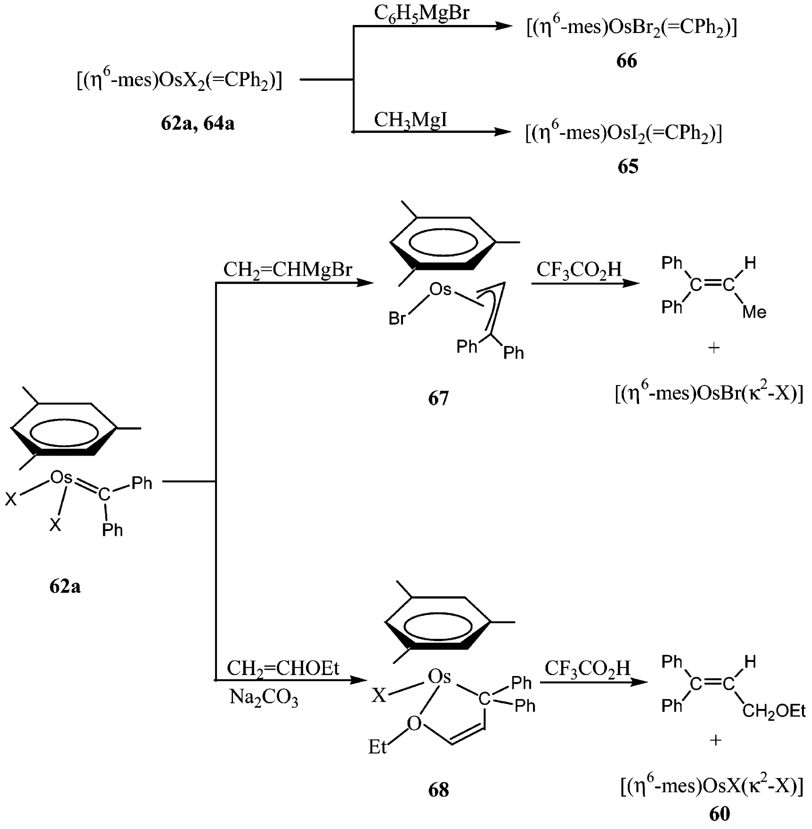
(54) Werner, H.; Stahl, S.; Kohlmann, W. *J. Organomet. Chem.* **1991**, *409*, 285−298.

(55) (a) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939−5940. (b) Roper, W. R. *J. Organomet. Chem.* **1986**, *300*, 167−190.

(56) Werner, H.; Stüer, W.; Wolf, J.; Laubender, M.; Weberndörfer, B.; Herbst-Irmer, C.; Lehmann, C. *Eur. J. Inorg. Chem.* **1999**, 1889−1897.

(57) Werner, H.; Wecker, U.; Schulz, M.; Stahl, S. *Organometallics* **1991**, *10*, 3278−3282.

Scheme 24[a]

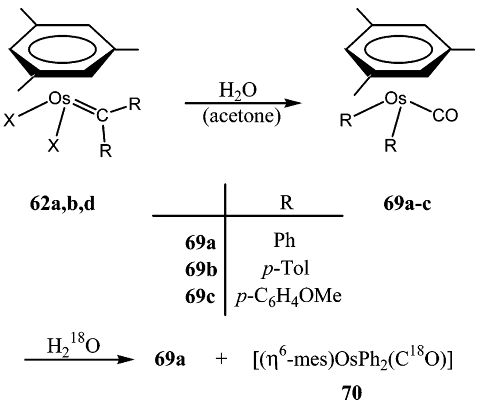


[a] Legend: X = CF_3CO_2.

which is followed by abstraction of a proton from the less electron-rich part of the bonded olefin with Na_2CO_3. The so-formed vinylic unit could then undergo an intramolecular C−C coupling with the CPh_2 group, similar to what probably occurs during the formation of **67**. Although d^6 transition-metal centers are not highly oxophilic, we assume that not only for steric but also for electronic reasons the five-membered OsC_3O ring is preferred compared to a four-membered OsC_3 cycle or an osmium η^3-allyl intermediate with an ethoxy substituent at the allyl group. Treatment of **68** with CF_3CO_2H leads to protolytic cleavage of the Os−C bond and to the formation of both the allyl ethyl ether $Ph_2C{=}CHCH_2OEt$ and the bis(trifluoroacetato) complex **60**.

By attempting to replace one carboxylato ligand in **62a**,**b**,**d** by a solvent molecule and to generate a possibly catalytically active $[(\eta^6\text{-mes})Os(\kappa^1\text{-}O_2CCF_3)(S)({=}CR_2)]^+$ (S = solvent) species, we observed an unusual C−C cleavage reaction for which, as far as we know, there is no precedent. The starting materials **62a**,**b**,**d** react with an excess of water in acetone solution to give, after chromatographic workup, the osmium(II) diaryl carbonyl compounds **69a**−**c**, which were isolated as yellow, moderately air-sensitive solids in 60−90% yield (Scheme 25).[53b] The diphenyl derivative **69a** was known and previously prepared from $[(\eta^6\text{-mes})OsCl_2(CO)]$ and C_6H_5Li.[58] On the basis of a labeling experiment with **62a** as the precursor and $H_2{}^{18}O$ as the substrate (affording a mixture of **69a** and **70** in a ratio of ca. 2:1),[53b] we feel that mechanistically the formation of **69a** is best understood if we assume that in the initial step the expected dissociation of one of the trifluoroacetate anions occurs, followed by an attack of the positively charged metal center on the ipso position of one phenyl group. The subsequent C−C bond cleavage could lead to a cationic $[Os](C_6H_5)(\equiv CC_6H_5)^+$ intermediate ($[Os] = (\eta^6\text{-mes})Os(\kappa^1\text{-}O_2CCF_3)$), which reacts with water by nucleophilic addition of OH^- to generate the osmium hydroxycarbene $[Os](C_6H_5)\{{=}C(OH)C_6H_5\}$. After dissociation of the remaining trifluoroacetate anion and abstraction of a proton (with Na_2CO_3) the osmium(II) benzoyl species $[(\eta^6\text{-mes})Os(C_6H_5)\{\kappa^2\text{-}C,O\text{-}C(Ph)O\}]$ could be formed, which after migration of the phenyl group from the benzoyl *C*(Ph)O carbon to the metal center yields the product. With regard to the postulated cationic intermediate formed initially, we note that a metallacyclopropene structure has also been discussed

Scheme 25[a]



[a] Legend: X = CF_3CO_2.

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(58) Werner, H.; Stahl, S.; Schulz, M. *Chem. Ber.* **1991**, *124*, 707−712.

in the context of the reactivity of related half-sandwich-type rhodium and molybdenum systems.[59,60] Moreover, Roper and co-workers reported[61] that the cationic carbyneruthenium complex $[RuCl(I)(\equiv CC_6H_5)(CO)(PPh_3)_2]^+$ reacts with water to give the ruthenium(II) phenyl derivative $[RuCl(C_6H_5)(CO)(PPh_3)_2]$, possibly via a series of steps analogous to those discussed for the formation of **69a**. To explain why in the reaction of **62a** with $H_2{}^{18}O$ the labeled compound **70** is not formed exclusively, we assume either that both $H_2{}^{18}O$ and unlabeled $CF_3CO_2{}^-$ attack the cationic osmium carbyne intermediate in parallel steps or that initially in a fast equilibrium trifluoroacetate reacts with $H_2{}^{18}O$ to give ^{18}O-labeled trifluoroacetate and $H_2{}^{16}O$, the latter being the substrate to form the carbonyl ligand with unlabeled oxygen.

Concluding Remarks

The work summarized in this review illustrates that half-sandwich-type complexes with non-Fischer-type carbene ligands and rhodium, iridium, ruthenium, and osmium as the metal centers are readily accessible and offer an interesting chemistry indeed. While the rhodium and iridium η^5-cyclopentadienyl and η^5-indenyl compounds with Rh=CRR′ and Ir=CRR′ as the molecular fragments are prepared from starting materials that already contain the carbene ligand, both the ruthenium η^5-cyclopentadienyl and η^5-indenyl complexes as well as the osmium η^6-arene derivatives are obtained from half-sandwich-type precursors which easily generate a labile intermediate that reacts with a diazoalkane to give the metal carbene by elimination of N_2. The reactions of the rhodium and iridium compounds $[(\eta^5\text{-}C_5H_5)M(=CRR')(L)]$ (M = Rh, Ir) and $[(\eta^5\text{-}C_9H_7)Rh(=CRR')(L)]$ with Lewis bases and acids lead to ligand substitution, protonation or alkylation of the carbene ligand, or, quite unexpectedly, migratory insertion of the CRR′ unit into one of the C−H bonds of the ring. A typical feature of the ruthenium complexes $[(\eta^5\text{-}C_5H_5)RuCl(=CRR')(L)]$ and $[(\eta^5\text{-}C_9H_7)RuCl(=CRR')(L)]$ is that they react with Grignard reagents and organolithium compounds by displacement of the chloride and subsequent C−C coupling to yield half-sandwich-type complexes with η^3-allyl, η^3-benzyl, and substituted olefins as ligands. With regard to the osmium arene carbenes, the most exciting result is that upon treatment of $[(\eta^6\text{-mes})OsX_2(=CR_2)]$ ($X = CF_3CO_2$, R = aryl) with water in acetone solution the $OsX_2(=CR_2)$ fragment is transformed into an $OsR_2(CO)$ moiety.

Although some of the half-sandwich-type metal carbenes react with olefins by incorporating the CRR′ unit into the product, the respective precursors are catalytically inactive in olefin metathesis. Even the ruthenium indenyl complexes containing a Ru=CHPh or $Ru=CHSiMe_3$ bond are inert in the presence of an excess of propene and styrene.[62] Despite this observation and our unsuccessful attempts to prepare the cationic half-sandwich-type ruthenium carbene $[(\eta^6\text{-arene})RuX(=CRR')(L)]^+$, the generation of such a species remains to be done. It is a particular challenge insofar as recent work by Dixneuf and Fürstner et al. revealed that the related allenylidene complexes $[(\eta^6\text{-arene})RuCl(=C=C=CPh_2)(PR_3)]^+$ proved to be excellent catalysts for ring-closing olefin metathesis.[63]

Acknowledgment. I thank first and foremost my co-workers in this field, in particular Dr. Elke Bleuel, Dr. Thomas Braun, Dr. Thomas Daniel, Dr. Rita Guerrero Sanchez, Dr. Gerhard Henig, Dr. Ulrich Herber, Dr. Dagmara A. Ortmann, Dr. Peter Schwab, Dr. Birgit Weberndörfer, Dr. Justin Wolf, and Mr. Gerhard Münch. Moreover, I acknowledge the indispensable contributions of other members of our group (Dr. Olaf Gevert, Dr. Kerstin Ilg, Dr. Matthias Laubender, Dr. Norbert Mahr, Dr. Paul Steinert, and Dr. Bettina Windmüller), who elucidated the crystal and molecular structures of the complexes reported. It was a pleasure to collaborate with Professor Martin Bennett and his group on the chemistry of the osmium arene carbenes. The constant and unbureaucratic financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG is also gratefully acknowledged.

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(59) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1983**, *243*, C63−C70.

(60) Feher, F. J.; Green, M.; Rodrigues, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1206−1208.

(61) Gallop, M. A.; Roper, R. W. *Adv. Organomet. Chem.* **1986**, *25*, 121−198.

(62) Münch, G. Unpublished results.

(63) (a) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 1315−1316. (b) Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1999**, 2249−2250. (c) Fürstner, A.; Liebl, M.; Lehmann, C. W.; Picquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem. Eur. J.* **2000**, *6*, 1847−1857.