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Vinylidene Compounds from the Reactions of $Me_3SiC{\equiv}CSiMe_3$ with $Tp^{Me2}Ir$ Precursors. Protonation to Alkylidene and Iridabenzene Structures

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Reaction of the Ir(I) butadiene compound $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ with the alkyne $Me_3SiC{\equiv}CSiMe_3$ gives the vinylidene $Tp^{Me2}Ir(CH_2C(Me){=}C(Me)CH_2)({=}C{=}C(SiMe_3)_2)$ (**1**). A related vinylidene **2** forms when $Tp^{Me2}Ir(Ph)_2(N_2)$ is reacted with $Me_3SiC{\equiv}CSiMe_3$. Compounds **1** and **2** have been characterized by microanalysis and spectroscopy (IR, ^1H and $^{13}C\{^1H\}$ NMR data), and in addition the molecular structure of **1** has been determined by X-ray diffraction. The reactions of these compounds with different protic acids have been investigated. Thus, the vinylidene **2** gives rise to the cationic alkylidene $[Tp^{Me2}Ir(Ph)(Et_2O)({=}C(Me)Ph)]BF_4$ (**3**) when treated with HBF_4, to the neutral chlorocarbene $Tp^{Me2}Ir(Ph)(Cl)({=}C(Me)Ph)$ (**4**) upon reaction with HCl, and to the neutral alkylidene $Tp^{Me2}Ir(Ph)(\kappa^1\text{-}O_2CCF_3)({=}C(Me)Ph)$ (**5**) by action of CF_3COOH. In turn the vinylidene species **1** and CF_3COOH give rise to the iridabenzene compound $Tp^{Me2}Ir(H)(CHC(Me)C(Me)CHC(Me))$ (**6**), characterized in the solid state by X-ray crystallography.

Introduction

Transition metal compounds with metal to carbon multiple bonds are of fundamental importance in chemistry. In particular those containing M═C bonds,[1] that is, the metal carbenes, vinylidenes (M═C═C), allenylidenes (M═C═C═C), and others, find widespread applications in chemical synthesis. Vinylidenes and allenylidenes are often generated in reactions of simple or functionalized alkynes with transition metal complexes. Different routes to vinylidene derivatives have been developed,[2] a straightforward procedure consisting in the activation of a terminal alkyne RC≡CH. The mechanism of the RC≡CH to :C═CHR rearrangement continues to attract theoretical and experimental interest. The reaction is thought to proceed with initial coordination of the alkyne, followed by either a direct 1,2-hydrogen shift or a C−H oxidative addition step.[3] The ability of the $SiMe_3$ or related groups to migrate (*β*-elimination[4] and sigmatropic shifts[5]) has been exploited by Werner and co-workers, and others, to prepare silyl-substituted vinylidenes $M{=}C{=}C(SiMe_3)R$ and $M{=}C{=}C(SiMe_3)_2$ in reactions involving alkynyl silanes $RC{\equiv}CSiMe_3$ and $Me_3SiC{\equiv}CSiMe_3$, respectively.[6]

In recent years we have prepared different $Tp^{Me2}Ir(III)$ carbenes (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) in reactions that involve multiple C−H bond activation.[7] In addition, we have investigated the reactivity of some unsaturated $Tp^{Me2}Ir$ reagents toward dimethylacetylene dicarboxylate and obtained metallacyclic structures resulting from the coupling of two or three molecules of the alkyne.[8] We were interested in extending the alkyne chemistry of $Tp^{Me2}Ir$ to the synthesis of vinylidene and allenylidene compounds. Using standard alkyne activation chemistry and the appropriate $Tp^{Me2}Ir(I)$ or $Tp^{Me2}Ir(III)$ precursors we have prepared the vinylidenes

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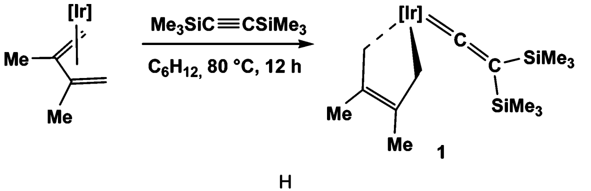
$Tp^{Me2}Ir(CH_2C(Me){=}C(Me)CH_2)({=}C{=}C(SiMe_3)_2)$ (**1**) and $Tp^{Me2}Ir(Ph)_2({=}C{=}C(SiMe_3)_2)$ (**2**) and have investigated their reactivity toward Brönsted acids. Thus upon reaction with trifluoroacetic acid, **1** converts into the iridabenzene complex **6** via a novel, unprecedented route, while **2** gives rise to alkylidenes **3**, **4**, and **5**, which contain an $[Ir]{=}C(Me)Ph$ unit, in its reactions with excess HBF_4, HCl, and CF_3COOH, respectively.

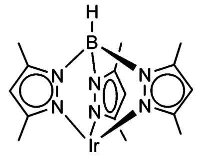
Results and Discussion

Treatment of the Ir(I) diene compound $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$[9] in cyclohexane with the alkynyl silane $Me_3SiC{\equiv}CSiMe_3$ (BTMSA) allows isolation of the iridium vinylidene **1** (eq 1).

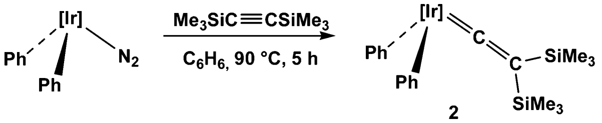


(1)

[Ir] = $Tp^{Me2}Ir$ =



The formation of **1** requires a significant electronic reorganization within the diene ligand that changes from $\eta^4{:}\pi,\pi$ to $\eta^2{:}\sigma,\sigma$, as well as a change in the formal oxidation state of the metal, from Ir(I) to Ir(III). We have demonstrated previously this kind of rearrangements in the reaction of various Ir(I) diene compounds with different Lewis bases.[10] On these grounds, it seems probable that the reaction of eq 1 proceeds through an Ir(III) alkyne complex intermediate that then experiences a 1,2-silyl shift to yield **1**. In accord with this hypothesis, the Ir(III) complex $Tp^{Me2}Ir(Ph)_2(N_2)$,[11] which possesses a labile dinitrogen ligand, reacts also with BTMSA to form a silyl-substituted vinylidene complex **2** related to **1** (eq 2).



(2)

The same complex **2** may alternatively be generated starting from the diene derivative $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ under the conditions of eq 2, using C_6H_6 as the solvent. In these circumstances, benzene reacts with the diene complex faster than BTMSA, extrudes the hydrocarbon, and generates the reactive unsaturated fragment $[Tp^{Me2}Ir(Ph)_2]$, subsequently trapped by the alkyne.

The vinylidenes **1** and **2** have been fully characterized by microanalysis and spectroscopy (IR, ^1H and ^{13}C NMR studies). In addition, the solid-state structure of **1** has been determined by X-ray crystallography. The stretching frequency of the C=C bond appears in both compounds around 1700 cm^{-1}, whereas the iridium-bound carbene carbon resonates at 261.5 (**1**) and 260.5 (**2**) ppm in the $^{13}C\{^1H\}$ NMR spectrum.[12,13] The β-carbon of the vinylidene linkage appears in the proximity of δ 89 for the two derivatives. In the ^1H NMR spectra of **1** and **2** the $SiMe_3$ are inequivalent and give rise to two shielded singlets around 0 ppm, due to lack of rotation of the Ir=C bond on the NMR time scale. Figure 1 shows an ORTEP view of a molecule of **1**, while Tables 1 and 2 present crystal data, and bond lengths and angles, respectively.

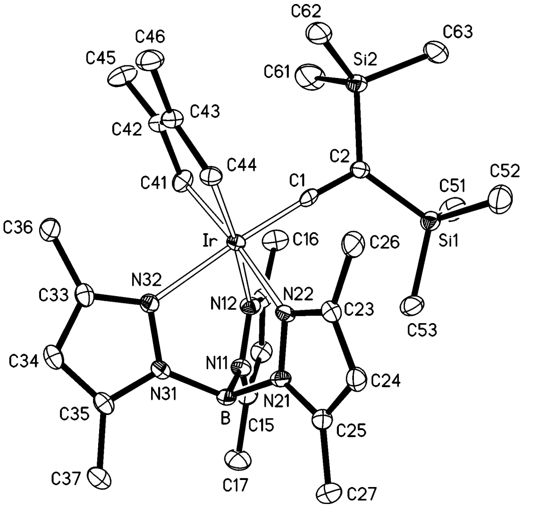


Figure 1. X-ray structure of complex **1** (thermal ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity).

The iridacyclopentene unit is planar, and it is characterized by a C−Ir−C bite angle of 82.62(14)°. The sp^3 carbon atoms bonded to iridium form iridium−carbon bonds with lengths that are identical within experimental error (ca. 2.08 Å). Their value is typical of an Ir−C single bond, while the shorter Ir−C separation of 1.83 Å found in the vinylidene unit is suggestive of some double-bond character. In the metallacyclopentene moiety, the carbon−carbon double bond between C(42) and C(43) is characterized by a distance of 1.326(5) Å, a value similar to the C(1)=C(2) bond of the vinylidene ligand (1.290(5) Å). The N−Ir−N angles within the $Tp^{Me2}Ir$ fragment have magnitudes close to 90°, and of the three Ir−N bonds, that *trans* with respect to the vinylidene ligand is slightly longer (2.20 Å) than the other two (2.17 Å).

Since it is well-known that the addition of electrophiles to vinylidenes is governed by the appreciable charge localization on the β vinylidene carbon atom,[12] we have studied the reactions of compounds **1** and **2** with protic acids. The protonation was expected to yield a cationic carbyne that could then experience migratory insertion chemistry, coupling with the hydrocarbyl ligands of **1** and **2**. In the case of **2**, the protonation to give the cationic alkylidene complex **3** (eq 3) can be carried out with different protic acids, e.g., HBF_4/Et_2O, HPF_6/H_2O, and $[H(OEt_2)_2][BAr'_4]$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$), but the best results have been obtained using ethereal solutions of HBF_4. Protonations with

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Table 1. Crystal Data and Data Collection and Refinement Details for 1, 5, and 6·1/2Et$_2$O

	1	**5**	**6**·1/2Et$_2$O
formula	$C_{29}H_{50}BIrN_6Si_2$	$C_{31}H_{35}BF_3IrN_6O_2$	$C_{25}H_{39}BIrN_6O_{0.5}$
mol wt	791.94	783.66	634.63
color, habit	yellow, block	dark red, block	green, blade
symmetry, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$	monoclinic, $C2/c$
a, Å	11.1757(7)	17.4856(13)	35.009(2)
b, Å	12.5388(8)	19.3601(14)	7.9680(5)
c, Å	24.6761(16)	20.1012(15)	25.7960(17)
β, deg	95.486(1)	109.392(1)	129.232(1)
V, Å^3	3442.0(4)	6418.7(8)	5573.9(6)
Z	4	8	8
D_{calcd}, g cm^{-3}	1.432	1.622	1.513
μ, mm^{-1}	3.975	4.215	4.816
2θ range, deg	4.6−60	4.2−60	4.7−60.1
temp, K	123(2)	173(2)	100(2)
no. of data collected	48 944	61 470	41 322
no. of unique data	9785 (R_{int} = 0.029)	18 492 (R_{int} = 0.051)	8030 (R_{int} = 0.037)
no. of params/restraints	366/0	808/272	324/1
R1^a ($F^2 > 2\sigma(F^2)$)	0.0357	0.0403	0.0375
wR2^b (all data)	0.0788	0.0991	0.0699

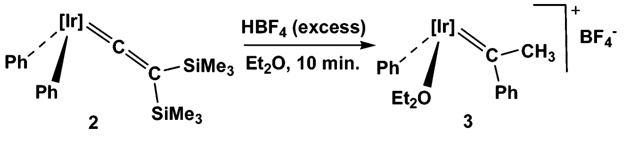
[a] $R1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Ir−C(1)	1.829(3)	C(1)−C(2)	1.290(5)
Ir−C(44)	2.075(3)	C(2)−Si(2)	1.889(4)
Ir−C(41)	2.082(4)	C(2)−Si(1)	1.892(4)
Ir−N(22)	2.172(3)	C(41)−C(42)	1.519(5)
Ir−N(12)	2.179(3)	C(42)−C(43)	1.326(5)
Ir−N(32)	2.202(3)	C(43)−C(44)	1.504(5)
C(1)−Ir−C(44)	91.02(14)	C(41)−Ir−N(12)	93.88(13)
C(1)−Ir−C(41)	91.51(15)	N(22)−Ir−N(12)	89.01(11)
C(44)−Ir−C(41)	82.62(14)	C(1)−Ir−N(32)	176.39(13)
C(1)−Ir−N(22)	94.45(12)	C(44)−Ir−N(32)	92.02(13)
C(44)−Ir−N(22)	94.01(13)	C(41)−Ir−N(32)	90.80(13)
C(41)−Ir−N(22)	173.20(13)	N(22)−Ir−N(32)	83.41(11)
C(1)−Ir−N(12)	93.47(13)	N(12)−Ir−N(32)	83.61(11)
C(44)−Ir−N(12)	174.38(13)		

the other acids specified above are less clean and generate different byproducts.

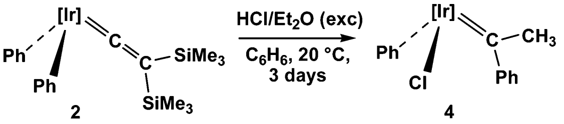
Interestingly, the reaction of **2** and HBF_4/Et_2O requires a 6-fold molar excess in order to proceed to completion; the use of a lower proportion of the acid gives the product **3** together with unreacted **2**. As discussed below, the two $SiMe_3$ groups of **2** are lost in the course of the reaction, and whereas their fate has not been ascertained, it is likely that an excess of the acid is needed in order to ensure the removal of these groups from the vinylidene terminus (eq 3).



(3)

The most characteristic spectroscopic feature of **3** is a deshielded $^{13}C\{^1H\}$ signal at 305.7 ppm attributable to the carbene carbon. A long-range $^1H-^{13}C$ heterocorrelation spectrum reveals that this iridium-bound carbon is bonded also to one methyl and one phenyl group, and therefore in addition to the loss of the silyl fragments one of the phenyl groups has migrated from the iridium to the unsaturated carbon atom bonded to the metal. ^1H NMR studies suggest that a molecule of ether completes the metal coordination, but this is not conclusive and the ether may be, in part, displaced by adventitious water. While in common with other cationic late transition metal compounds that contain weakly bound solvent molecules satisfactory microanalytical data have not been obtained,[14] the similarity of the NMR data of **3** with those discussed below for the closely related compounds **4** and **5** strongly supports the proposed formulation. Additional evidence for the suggested structure comes from the clean conversion of **3** into **4** upon reaction with bis(triphenylphosphine)iminium chloride, PPN^+Cl^- (see Experimental Section).

To avoid the above problem and obtain isolable neutral carbenes related to **3**, the protonation of **2** was carried out using HCl and CF_3COOH, as Brönsted acids with coordinating anions. As shown in eq 4 for the HCl reaction, an excess of the acid is needed, but the resulting compound **4** contains a chloride ligand in place of the molecule of Et_2O/H_2O. In contrast with **3**, the neutral alkylidene **4** is a microcrystalline compound that has been isolated in analytically pure form. The reaction with CF_3COOH is considerably faster and appears to be complete after stirring, for 2 h at room temperature, a tetrahydrofuran solution of the iridium precursor and the acid. The resulting compound, $Tp^{Me2}Ir(Ph)(\kappa^1\text{-}O_2CCF_3)(=C(Me)Ph)$ **5**, contains a monodentate trifluoroacetate ligand (see below).



(4)

The carbene part of **4** and **5** is identical to that of **3**, and its carbene carbon has a very similar chemical shift, resonating at 303.3 (**4**) and 305.7 (**5**) ppm. Other resonances associated with the alkylidene moiety of **4** and **5** match closely those of **3**. For instance, the methyl protons have chemical shift values in the short range from 2.80 to 3.01 ppm for the three compounds, whereas the corresponding $^{13}C\{^1H\}$ signals are located at δ 48 (**3**), 51.3 (**4**), and 46.5 (**5**) ppm. An additional similarity is the observation of sterically hindered rotation around the C−Ph bond within the =C(Me)Ph alkylidene unit of the three compounds, responsible for the broadness (in some cases complete disappearance) of some of the ^1H and $^{13}C\{^1H\}$ aromatic resonances (see Experimental Section).

Monodentate coordination of the trifluoroacetate ligand of **5** is hinted by the observation of bands at ca. 1725 and 1420 cm^{-1} for the asymmetric and symmetric stretching vibrations of the

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(14) For a recent example illustrating this difficulty see: Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Modrego, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2005**, *127*, 11184.

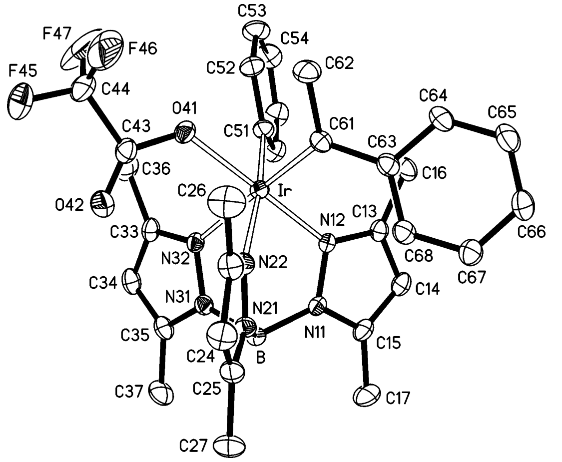


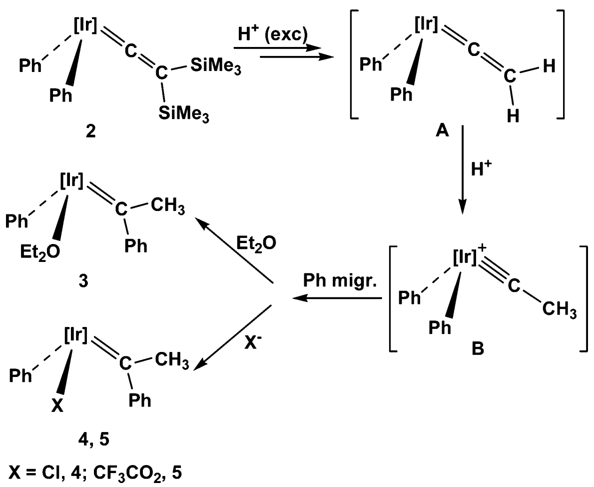
Figure 2. X-ray structure of complex **5** (thermal ellipsoids drawn at the 30% probability level, hydrogen atoms omitted for clarity).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 5

Ir−C(61)	1.927(4)	Ir−C(51)	2.064(4)
Ir−O(41)	2.070 (3)	C(61)−C(62)	1.506(6)
Ir−N(22)	2.130(3)	C(61)−C(63)	1.473(6)
Ir−N(12)	2.036(3)	O(41)−C(43)	1.294(5)
Ir−N(32)	2.160(4)	O(42)−C(43)	1.186(6)
C(61)−Ir−N(12)	93.14(16)	C(51)−Ir−N(22)	172.04(16)
C(61)−Ir−C(51)	94.30(18)	O(41)−Ir−N(22)	92.53(13)
N(12)−Ir−C(51)	91.21(15)	C(61)−Ir−N(32)	178.21(15)
C(61)−Ir−O(41)	89.43(16)	N(12)−Ir−N(32)	86.32(13)
N(12)−Ir−O(41)	176.36(13)	C(51)−Ir−N(32)	87.42(16)
C(51)−Ir−O(41)	86.02(15)	O(41)−Ir−N(32)	91.19(13)
C(61)−Ir−N(22)	93.52(16)	N(22)−Ir−N(32)	84.78(14)
N(12)−Ir−N(22)	89.88(13)		

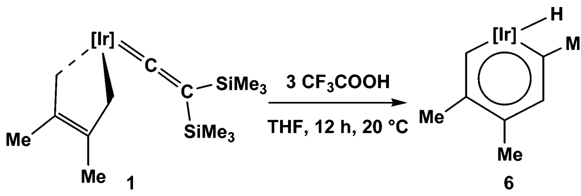
carboxylate OCO moiety, with a difference of 305 cm^{-1}. These data are similar to those found for κ^1-O_2CCF_3 coordination in somewhat related compounds.[15] Single-crystal X-ray studies validate this proposal. Figure 2 shows an ORTEP view of the molecules of **5**, while Tables 1 and 3 provide crystal data, and bond lengths and angles, respectively. As represented in Figure 2, the Tp^{Me2} ligand of **5** exhibits its common κ^3-coordination, binding to the Ir(III) unit through the three pyrazolyl units with Ir−N distances of 2.036(3), 2.130(3), and 2.160(4) Å. The carboxylate part of the CF_3CO_2 ligand binds to iridium through O41, with an Ir−O distance of 2.070(3) Å, and it is further characterized by C43−O41 and C43−O42 distances of 1.294(5) and 1.186(6) Å, respectively. As expected, the Ir−C51 distance to the coordinated Csp^2 carbon of the phenyl group, 2.064(4) Å, is significantly longer than the Ir−C61 distance of 1.927(4) Å to the carbon atom of the alkylidene unit.

Scheme 1



Since as pointed out above an excess of the acid is needed in order to convert compound **2** into **3**−**5**, it seems likely that a reactive, undetected vinylidene species (**A** in Scheme 1) is generated at the early stages of the reaction. Further action of the acid would result in the formation of the also undetected and highly reactive cationic bis(phenyl) ethylidyne species[16] **B** of Scheme 1, which could subsequently rearrange by migratory insertion of one of the phenyl groups onto the carbyne carbon. This rearrangement involves the formation of a new C−C bond, and in all probability it must be an irreversible step. Coordination of the Lewis base (Et_2O or X^-) to the unsaturated metal center leads to the observed products **3**−**5**. Although the chloride anion present in the reaction mixture could compete with the phenyl group to bind to the carbene carbon of the product,[17] we have not detected the chlorocarbene product in this reaction.

The reaction of vinylidene **1** with acids is also dependent upon the reagent employed. Thus, while HCl/Et_2O, HBF_4/Et_2O, and others give complex mixtures of products, treatment of **1** with trifluoroacetic acid under the conditions of eq 5 allows isolation of complex **6** in about 80% yield. Substitution of THF by Et_2O as the reaction solvent has a negative effect, as the yield of **6** decreases substantially and moreover significant amounts of an unidentified byproduct are also generated.



(5)

Compound **6** has been unequivocally characterized as an iridabenzene structure with the aid of NMR studies and X-ray crystallography. Figure 3 shows an ORTEP view of the molecule of **6**, while Tables 1 and 4 provide crystal data, and bond lengths and angles, respectively. **6** adds to a growing family of irida aromatic species that have been prepared by different researchers,[18] including ourselves.[19] The ring carbon atoms bonded to the metal give rise to $^{13}C\{^1H\}$ signals at 235.8 and 209.0 ppm (Ir−*C*(Me) and Ir−*C*(H), respectively), i.e., in a region typical of Ir−C multiple bonds. Similarly in the ^1H NMR spectrum the signal corresponding to the Ir−CH proton appears at 14.01 ppm, a value close to those found for iridium alkylidenes $Tp^{Me2}Ir{=}CHR$[20] and for other iridabenzene structures.[21]

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[15] Werner, H.; Ilg, K.; Weberndörfer, B. *Organometallics* **2000**, *19*, 3145.

[16] Luecke, H. F.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 11008.

[17] (a) Wolf, J.; Stüer, W.; Grünwald, C.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1124. (b) Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, *15*, 1960. (c) González-Herrero, P.; Weberndörfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 3672.

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[19] (a) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Salazar, V.; Oñate, E.; Mereiter, K. *J. Am. Chem. Soc.* **2003**, *125*, 9898. (b) Álvarez, E.; Paneque, M.; Poveda, M. L.; Rendón, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 474.

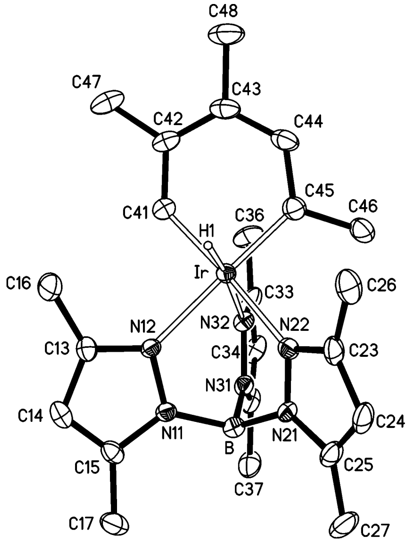


Figure 3. X-ray structure of complex **6** (thermal ellipsoids drawn at the 40% probability level, hydrogen atoms omitted for clarity except the hydride ligand).

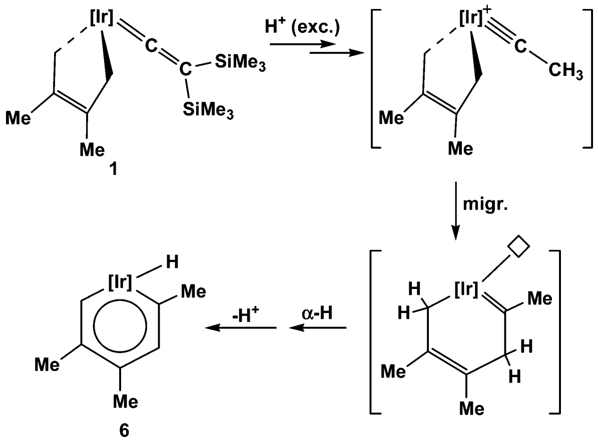
Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 6 in 6·1/2Et₂O

Ir−C(45)	1.939(4)	Ir−H	1.50
Ir−C(41)	1.945(4)	C(41)−C(42)	1.388(6)
Ir−N(22)	2.152(3)	C(42)−C(43)	1.401(7)
Ir−N(12)	2.162(3)	C(43)−C(44)	1.392(7)
Ir−N(32)	2.162(3)	C(44)−C(45)	1.397(6)
C(45)−Ir−C(41)	88.83(18)	N(22)−Ir−N(32)	87.09(13)
C(45)−Ir−N(22)	95.90(16)	N(12)−Ir−N(32)	84.69(12)
C(41)−Ir−N(22)	170.76(15)	C(45)−Ir−H(1)	91(2)
C(45)−Ir−N(12)	178.13(16)	C(41)−Ir−H(1)	83(1)
C(41)−Ir−N(12)	92.77(15)	N(22)−Ir−H(1)	89(1)
N(22)−Ir−N(12)	82.38(12)	N(12)−Ir−H(1)	88(2)
C(45)−Ir−N(32)	95.97(16)	N(32)−Ir−H(1)	172(2)
C(41)−Ir−N(32)	100.34(14)		

In the solid state the molecules of **6** have a distorted octahedral geometry characterized by three very similar Ir−N bonds (ca. 2.16 Å) and by two Ir−C(sp^2) bonds that are identical within experimental error (1.94 Å). Comparison with the Ir−C bonds of different kinds present in **1** is appropriate and reveals that the two Ir−C bonds of **6** have intermediate length between the Ir−C single bonds of the iridacyclic unit of **1** (2.08 Å) and the Ir−C multiple bond of the vinylidene terminus (1.83 Å). The metallacyclic part of **6** is almost planar, the deviation of the metal atom from the mean plane defined by the five carbon atoms being of 0.50 Å. The rms aplanarity of the five ring carbon atoms is 0.009 Å.

The structural analogy of **1** and **2** hints at similar reaction pathways for their protonation to **6** and **4**/**5**, respectively. On these grounds Scheme 2 shows a reasonable reaction path to the iridacyclic compound **6**. As before, a cationic ethylidyne species is proposed as an unobserved intermediate. Migration of one of the alkyl termini of this species onto the unsaturated carbyne carbon atom and two proton rearrangements, namely, a α-H elimination and loss of a proton (in either order), would then account for the formation of **6**.

Scheme 2



Conclusions

In conclusion, iridium vinylidene species stabilized by the ancillary Tp^{Me2} ligand are accessible from suitable Tp^{Me2}Ir(I) and Tp^{Me2}Ir(III) precursors in reactions with the alkyne $Me_3SiC{\equiv}CSiMe_3$. The $Ir{=}C{=}C(SiMe_3)_2$ linkages of the vinylidenes described are protonated by protic acids with loss of the silyl substituents. Reactive carbyne derivatives are proposed as key intermediates, and it is suggested that they rearrange by migratory insertion chemistry to the final products of the reactions, viz., the alkylidene compounds **3**, **4**, and **5** and the iridabenzene **6**.

Experimental Section

General Procedures. Microanalyses were by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained from a Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free dinitrogen, following conventional Schlenk techniques. The complexes $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$[9] and $Tp^{Me2}Ir(C_6H_5)_2N_2$[11] were obtained by published procedures.

$Tp^{Me2}Ir(\overline{CH_2C(Me){=}C(Me)CH_2})({=}C{=}C(SiMe_3)_2)$ (1). Compound $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (0.5 g, 0.87 mmol) and $Me_3SiC{\equiv}CSiMe_3$ (0.3 mL, 1.31 mmol) were dissolved in cyclohexane (8 mL), and the solution was stirred at 80 °C for 12 h. The volatiles were removed under reduced pressure, and quantitative conversion into **1** was ascertained by ^{1}H NMR. This complex was crystallized from a 1:1 Et_2O/pentane mixture at −20 °C (yellow crystals, 0.53 g, ca. 80%). ^{1}H NMR ($CDCl_3$): δ 5.78, 5.64 (s, 2:1, 3 CH_{pz}), 3.39, 2.49 (br d, AB spin system, 4 H, $^2J_{AB} = 13.8$ Hz, 2 $Ir{-}CH_2$), 2.59, 2.35, 2.29, 1.94 (s, 2:2:1:1, 6 Me_{pz}), 1.66 (s, 6 H, 2 CMe), 0.24, −0.34 (s, 9 H each, 2 $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 261.5 (Ir=C), 151.4, 151.0, 143.3, 143.0 (2:1:1:2, C_{qpz}), 140.2 (*C*Me), 108.1, 107.1 (1:2, CH_{pz}), 89.1 (*C*($SiMe_3)_2$), 19.2 (C*Me*), 14.8, 13.3, 12.9, 11.3 (2:1:2:1, Me_{pz}), 12.2 ($Ir{-}CH_2$, $^1J_{CH} = 125$ Hz), 3.7, 0.9 ($SiMe_3$). IR (Nujol): ν(C=C) 1705 cm^{-1}. Anal. Calcd for $C_{29}H_{50}BN_6Si_2Ir$: C, 46.9; H, 6.8; N, 11.3. Found: C, 46.8; H, 6.5; N, 11.4.

$Tp^{Me2}Ir(Ph)_2({=}C{=}C(SiMe_3)_2)$ (2). A solution of $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (0.207 g, 0.36 mmol) in benzene (10 mL) was treated with $Me_3SiC{\equiv}CSiMe_3$ (0.125 mL, 0.54 mmol). The reaction mixture was heated at 90 °C under dinitrogen (sealed

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(20) (a) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2158. (b) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. *Helv. Chim. Acta* **2001**, *84*, 2868. (c) Santos, L. L.; Mereiter, K.; Paneque, M.; Slugovc, C.; Carmona, E. *New J. Chem.* **2003**, *27*, 107. (d) Paneque, M.; Poveda, M. L.; Santos, L. L.; Salazar, V.; Carmona, E. *Chem. Commun.* **2004**, 1838.

(21) See for example: Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606.

ampoule) for 5 h, during which time it turned green. The solvent was evaporated, 20 mL of petroleum ether added, and the resulting solution concentrated and cooled to −20 °C. The green precipitate was separated from the mother liquor and dried in vacuo (0.17 g, ca. 60%). The mother liquor was concentrated and cooled to −20 °C, to obtain a second crop of the product, giving a total yield of 0.21 g, ca. 73%. As an alternative procedure, a solution of $Tp^{Me2}Ir(Ph)_2N_2$ (0.02 g, 0.03 mmol) and $Me_3SiC{\equiv}CSiMe_3$ (0.007 mL, 0.03 mmol) in benzene (10 mL) was heated at 90 °C for 25 min in a sealed ampoule under an atmosphere of argon. Following workup as above a green solid with identical spectroscopic data was obtained. ^1H NMR ($CDCl_3$): δ 8.18, 7.04, 6.87, 6.71, 6.57 (d, t, t, t, d, 2 H each, $^3J_{HH} \approx 7.3$ Hz, 10 CH_{ar}), 5.80, 5.70 (s, 2:1, 3 CH_{pz}), 2.47, 1.76, 0.89 (s, 3:2:1, 6 Me_{pz}), 0.57, −0.32 (s, 9 H each, 2 $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 260.5 (Ir=C), 151.2, 143.1, 142.7 (3:2:1, C_{qpz}), 140.8, 139.9, 126.0, 125.3, 121.6 (CH_{ar}), 132.8 (C_{qar}), 107.3, 107.2 (1:2, CH_{pz}), 89.0 ($C(SiMe_3)_2$), 14.9, 14.8, 13.3, 13.2 (1:2:1:2, Me_{pz}), 4.8, 1.6 ($SiMe_3$). IR (Nujol): ν(C=C) 1702 cm^{-1}. Anal. Calcd for $C_{35}H_{50}BN_6Si_2Ir$: C, 51.7; H, 6.2; N, 10.3. Found: C, 51.5; H, 6.1; N, 10.5.

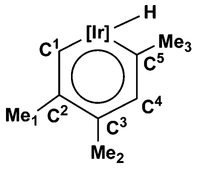
$[Tp^{Me2}Ir(Ph)(Et_2O)({=}C(Me)Ph)]BF_4$ (3). A solution of **2** (0.059 g, 0.07 mmol) in Et_2O (10 mL) was treated with HBF_4 (0.07 mL, 0.42 mmol, 54% in Et_2O) and stirred for 10 min at room temperature. The solvent was evaporated to yield a red oily residue, which was then dissolved in 1 mL of CH_2Cl_2 and treated with 10 mL of petroleum ether. A brick-red solid began to precipitate. The suspension was concentrated and cooled to −20 °C, and the solid was separated from the mother liquor and dried in vacuo. Yield: 0.036 g, ca. 62%. ^1H NMR ($CDCl_3$): δ 7.92, 7.31, 6.91, 6.69, 5.58 (d, dt, t, dt, d, 1 H each, $^3J_{HH} \approx 7.5$, $^4J_{HH} \approx 1.2$ Hz, 5 CH_{ar}, Ir−Ph), 7.58, 7.05 (br t, br s, 1:2, 3 CH_{ar}, Ir=C−Ph, the two remaining Ir=C−Ph resonances must be too broad to be located), 5.88, 5.74, 5.51 (s, 1 H each, 3 CH_{pz}), 2.84 (s, 3 H, Ir=C−Me), 2.58, 2.55, 2.45, 1.70, 1.39, 0.42 (s, 3 H each, 6 Me_{pz}). Signals at 3.90 (br) and 1.31 (t) (2:3 ratio) may be assigned to the CH_2 and CH_3 groups of the coordinated molecule of Et_2O. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 305.3 (Ir=C), 160.0 (C_{qar}(C−Ph)), 153.6, 151.7, 151.3, 145.6, 144.7 (1:1:1:2:1, C_{qpz}), 138.3, 133.1, 127.3, 126.8, 124.6 (CH_{ar}(Ir−Ph)), 130.7 (C_{qar}(Ir−Ph)), 134.7, 133.1 (1:2, CH_{ar}(C−Ph), the two remaining CH_{ar}(C−Ph) have not been located), 109.1, 108.3, 108.1 (CH_{pz}), 48.0 (Ir=C−*Me*), 15.0, 13.2, 12.5, 11.8 (1:1:3:1, Me_{pz}). Signals at 67.4 (br) and 14.0 (br) could be assigned to the CH_2 and CH_3 groups of coordinated Et_2O, respectively. The compound loses readily the coordinated molecule of Et_2O; it is possibly replaced by adventitious water. For this reason satisfactory microanalytical data could not be obtained.

$Tp^{Me2}Ir(Ph)(Cl)({=}C(Me)Ph)$ (4). Compound **2** (0.32 g, 0.39 mmol) was dissolved in Et_2O (5 mL), and HCl (12 mL, 1 M in Et_2O) was added. The solution was stirred at 20 °C for 72 h, and the volatiles were evaporated under vacuo. NMR monitoring of the crude product revealed the presence of **4** in almost quantitative yield (>90%). **4** was purified by column chromatography on silica gel, using a 2:1 mixture of hexane/Et_2O as eluent. It can be crystallized from hexane/Et_2O mixtures (2:1) at −20 °C. Yield: 0.11 g, ca. 40%. ^1H NMR ($CDCl_3$): δ 8.35, 7.23, 6.84, 6.61, 5.74 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx 7.5$ Hz, 5 CH_{ar}, Ir−Ph), 7.46, 7.04, 6.87 (t, br hump, br hump, 1:2:2, $^3J_{HH} \approx 7.5$ Hz, 5 CH_{ar}, Ir=C−Ph), 5.83, 5.69, 5.49 (s, 1 H each, 3 CH_{pz}), 3.01 (s, 3 H, Ir=C−Me), 2.55, 2.43, 1.90, 1.66, 0.43 (s, 2:1:1:1:1, 6 Me_{pz}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 303.3 (Ir=C), 161.0 (C_{qar}(C−Ph)), 154.6, 151.6, 151.0, 144.3, 144.1, 143.4 (C_{qpz}), 139.2, 137.8, 125.7, 125.3, 123.1 (CH_{ar}(Ir−Ph)), 133.0, 128.0 (1:2, CH_{ar}(C−Ph), the two remaining CH_{ar}(C−Ph) have not been located), 131.7 (C_{qar}(Ir−Ph)), 108.7, 108.1, 107.5 (CH_{pz}), 51.3 (Ir=C−*Me*, $^1J_{CH} = 128$ Hz), 15.1, 13.7, 13.2, 13.1, 12.6 (1:1:1:1:2, Me_{pz}). Anal. Calcd for $C_{29}H_{35}N_6ClBIr$: C, 49.3; H, 5.0; N, 11.9. Found: C, 49.5; H, 5.1; N, 12.3.

Reaction of 3 with PPNCl to Yield 4. A dichloromethane solution of the cationic complex **3**, generated as above, was reacted with PPN^+Cl^-, at 60 °C, for a period of 4 days. A clean transformation ensues, as revealed by ^1H and ^{13}C NMR studies of the reaction mixture, yielding the chloro alkylidene compound **4** as the major product of the reaction (≥80%).

$Tp^{Me2}Ir(Ph)(\kappa^1\text{-}O_2CCF_3)({=}C(Me)Ph)$ (5). Compound **2** (0.11 g, 0.13 mmol) was dissolved in THF (8 mL), and CF_3COOH (0.03 mL) was added. The solution was stirred at 20 °C for 2 h, and the volatiles were evaporated under vacuo. NMR monitoring of the crude product revealed the presence of **5** in 85% spectroscopic yield. **5** was purified by column chromatography on silica gel, using a 15:1 → 1:1 mixture of hexane/Et_2O as eluent (yield of 60%). It can be crystallized from hexane/Et_2O mixtures (2:1) at −20 °C. ^1H NMR ($CDCl_3$): δ 8.23, 7.26, 6.88, 6.66, 5.72 (d, t, t, t, d, 1 H each, $^3J_{HH} \approx 7.5$ Hz, 5 CH_{ar}, Ir−Ph), 7.51, 7.03, 6.93 (t, br hump, br hump, 1:2:2, $^3J_{HH} \approx 7.5$ Hz, 5 CH_{ar}, Ir=C−Ph), 5.78, 5.65, 5.51 (s, 1 H each, 3 CH_{pz}), 2.80 (s, 3 H, Ir=C−Me), 2.56, 2.55, 2.44, 1.47, 1.23, 0.46 (s, 3 H each, 6 Me_{pz}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 305.7 (Ir=C), 160.9 (O*C*OCF$_3$, $^2J_{CF} = 36.1$ Hz), 160.6 (C_{qar}(C−Ph)), 153.7, 151.4, 150.4, 144.7, 144.1, 143.6 (C_{qpz}), 138.7, 134.9, 126.1, 125.3, 123.5 (CH_{ar}(Ir−Ph)), 133.5, 128.2 (1:2, CH_{ar}(C−Ph), the two remaining CH_{ar}(C−Ph) have not been located), 133.1 (C_{qar}-(Ir−Ph)), 113.6 (OCO*C*F$_3$, $^1J_{CF} = 292$ Hz), 107.9, 107.5, 107.1 (CH_{pz}), 46.5 (Ir=C−*Me*), 15.3, 13.2, 12.5, 11.6, 11.4 (1:1:2:1:1, Me_{pz}). IR (Nujol): $\nu(OCO_{as})$ 1727, $\nu(OCO_s)$ 1418 cm^{-1}. Anal. Calcd for $C_{31}H_{35}N_6F_3O_2BIr$: C, 47.5; H, 4.5; N, 10.7. Found: C, 47.5; H, 4.6; N, 10.6.

$Tp^{Me2}\overline{Ir(H)(CHC(Me)C(Me)CHC}(Me))$ (6). To a solution of compound **1** in THF (0.2 g, 0.27 mmol; 7 mL) was added 3 molar equiv of CF_3COOH (62.3 μL). The resulting solution was stirred at room temperature for 12 h, and the volatiles were removed under vacuo. NMR analysis of the crude product revealed the presence of **6** in almost quantitative yield (>90%). Complex **6** can be obtained from diethyl ether at −20 °C as green crystals of the solvate **6**·1/2Et_2O, which was used for X-ray analysis.



^1H NMR ($CDCl_3$): δ 14.01 (s, 1 H, C^1H), 6.86 (s, 1 H, C^4H), 5.85, 5.84, 5.55 (s, 1 H each, 3 CH_{pz}), 2.44, 2.27, 2.09, 0.92 (s, 3 H each, 4 Me_{pz}), 2.40, 2.39, 2.38 (s, 3 H each, 2 Me_{pz}, Me_1), 2.12 (s, 3 H, Me_3), 1.88 (s, 3 H, Me_2), −22.04 (s, 1 H, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 235.8 (C^5), 209.0 (C^1, $^1J_{CH} = 135$ Hz), 163.0 (C^3), 151.8, 151.3, 149.7, 144.4, 144.1, 143.0 (C_{qpz}), 135.7 (C^4, $^1J_{CH} = 149$ Hz), 134.3 (C^2), 106.2, 105.9, 105.3 (CH_{pz}), 41.6 (Me_3), 25.6 (Me_2), 22.2 (Me_1), 16.0, 15.5, 12.8, 12.6, 12.6, 10.4 (Me_{pz}). IR (Nujol): ν (Ir−H) 2134 cm^{-1}. Anal. Calcd for $C_{23}H_{34}N_6BIr$: C, 46.2; H, 5.7; N, 14.1. Found: C, 46.1; H, 5.7; N, 13.7.

X-ray Crystal Structure Analyses. Suitable crystals grown from diethyl ether/pentane (**1**), diethyl ether/hexane (**5**), or diethyl ether (**6**) were selected. X-ray data were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å, and 0.3° ω-scan frames covering complete spheres of the reciprocal space. Corrections for absorption and $\lambda/2$ effect were applied.[22] After structure solution with the program SHELXS97, structure refinements on F^2 were carried out with the program SHELXL97.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in

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[22] Bruker programs: *SMART*, version 5.054; *SAINT*, version 6.2.9; *SADABS*, version 2.03; *XPREP*, version 5.1; *SHELXTL*, version 5.1; Bruker AXS Inc.: Madison, WI, 2001.

idealized positions and were refined riding with the atoms to which they were bonded. CH_3 were allowed to rotate about the C−C bonds, and the hydride in **6** was refined with a Ir−H distance constraint of 1.50 Å. Compound **6** contained in the solid state disordered diethyl ether located in channels extending parallel to the *b*-axis. This solvent was taken into account by seven peaks that were refined as carbon atoms with population parameters varied. The idealized chemical formula is **6**·1/2Et_2O. Crystal data and further experimental details are summarized in Table 1.

Acknowledgment. Financial support from the Spanish Ministerio de Educación y Ciencia (MEC) (CTQ2004-00409/BQU, FEDER support) and from the Junta de Andalucía, and EU COST Action WD-D17-003 are acknowledged. N.R. and L.L.S. thank the MEC for a grant.

Supporting Information Available: Complete crystallographic data and technical details in CIF format for compounds **1**, **5**, and **6**·1/2Et_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050634K

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(23) Sheldrick, G. M. *SHELX97*: Program System for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997.