from 1-indanone was also reduced in high enantioselectivity using the Rh–(*R*,*S*,*R*,*S*)-Me-PennPhos complex (entry 2) while *ee* values achieved with either Rh–BINAP or Rh–Me-DuPhos complexes were significantly lower (entries 3 and 4). Hydrogenation of a substituted 3,4-dihydronaphth-1-yl acetate gave outstanding enantioselectivities with the Rh–(*R*,*S*,*R*,*S*)-Me-PennPhos catalytic system (entries 5 and 6). The highly enantioselective hydrogenation of five- and six-membered ring enol acetates provides a practical route for the syntheses of the corresponding chiral secondary alcohols.

Several acyclic enol acetates were also hydrogenated with the Rh–(*R*,*S*,*R*,*S*)-Me-PennPhos catalyst (entries 7–13). The enantioselectivities were lower than those achieved with cyclic enol acetates. Modifying the steric or electronic properties of these acyclic enol acetates had only small effects on the enantioselectivities (observed ranging from 80 to 85% *ee*). For the enol acetate derived from acetophenone, the enantioselectivity obtained with Rh–(*R*,*S*,*R*,*S*)-Me-PennPhos (entries 7 and 8) was comparable to those obtained with Rh–DuPhos compounds (77% *ee* in THF catalyzed by [Rh(Me-DuPhos)(cod)]BF_4, 89% *ee* in MeOH with [Rh(Me-DuPhos)(cod)]OTf,[3f] OTf = trifluormethanesulfonate). Further modification of the Rh–PennPhos structure may lead to practical catalysts for the hydrogenation of electron-rich acyclic enol acetates.

The rationale for the highly enantioselective hydrogenation of cyclic enol acetates is not clear. Phosphabicyclo[2.2.1]heptanes are electron-rich and conformationally rigid ligands with a well-defined deep chiral pocket. Our previous work has shown that this novel motif imparts valuable properties to this catalytic system.[4] Since enol acetates are likely to be chelating substrates, the constrained geometry of the cyclic enol acetates may enhance recognition toward chiral transition metal complexes compared with acyclic enol acetates.

Experimental Section

All reactions and manipulations were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Toluene and THF were distilled from sodium benzophenone ketyl under nitrogen. CH_2Cl_2 was distilled from CaH_2. MeOH was distilled from Mg under nitrogen. The chiral PennPhos ligand was prepared as previously described.[4c] Gas chromatography was carried out on Helwett-Packard 5890 and 6890 gas chromatographs using the Chiral Select 1000 column (15 m × 0.25 mm (inner diameter), carrier gas: He (1 mL min^{-1})).

General procedure for the asymmetric hydrogenation: To a solution of [$Rh(cod)_2$]BF_4 (5.0 mg, 0.012 mmol) in MeOH (10 mL) in a glovebox was added (*R*,*S*,*R*,*S*)-Me-PennPhos (0.15 mL of a 0.1 M solution in MeOH, 0.015 mmol). After the mixture was stirred for 30 min, the enol acetate (1.2 mmol) was added. The hydrogenation was performed at room temperature under 1.7 bar of hydrogen for 24 h. After the hydrogen was released, the reaction mixture was passed through a short silica gel column to remove the catalyst. The enantiomeric excess was measured by capillary GC without any further purification. The absolute configurations of the products were determined by comparing the observed optical rotations with those of chiral acetates made from readily available secondary alcohols.

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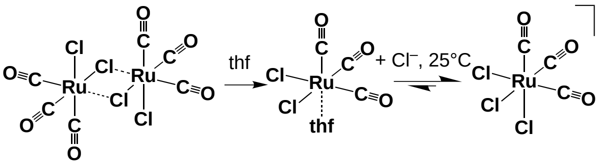
Reactions of a Transient Carbonyl(chloro)(hydrido)ruthenium(II) Complex with Ethylene, Alkynes, and CO; Chemistry of the New Anion [$Ru_2(CO)_4Cl_5$]$^-$**

Matthieu Faure, Luc Maurette, Bruno Donnadieu, and Guy Lavigne*

Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

In spite of the high interest in halide salts as promoters for a variety of carbon–carbon bond-forming reactions,[1–4] little is known about the reactivity of simple carbonyl(halo)ruthenium(II) complexes such as the interconvertible species **1**–**3** (Scheme 1).[5]



1 **2** **3**

Scheme 1.

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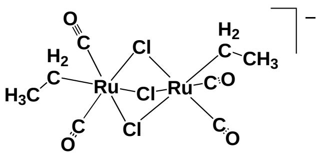
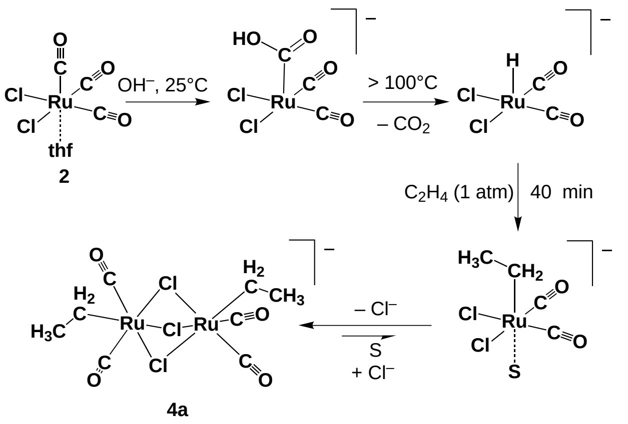


4a

It was previously shown that $[(PPh_3)_2N][Ru(CO)_3Cl_3]$ ([PPN]-**3**) is a catalyst precursor for the hydroesterification of ethylene with alkyl formates.[3d,e] More recently, Fabre et al.[6] made the intriguing observation that a novel, and yet very simple alkyl(carbonyl)(chloro)ruthenium(II) complex $[(PPh_3)_2N][Ru_2(\mu\text{-}Cl)_3(CO)_4(CH_2CH_3)_2]$ ([PPN]-**4a**) is produced in the reactor, and we believe this to be the resting state of the catalyst.

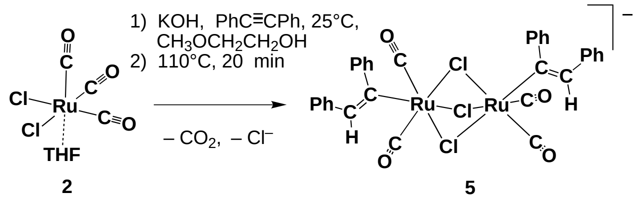
Assuming the anion **4a** results from the insertion of ethylene into an Ru–H bond of a precursor hydrido complex, we were challenged to devise a rational route to such a species in the absence of formate and to examine its aptitude to undergo insertion reactions with representative unsaturated organic substrates. Our approach (Scheme 2) is based in part on the principle of the water gas shift reaction.[7]



Scheme 2. Strategy for the synthesis of the ethyl complex **4a**. S = solvent.

Treatment of a solution of **2** in 2-methoxyethanol with one equivalent of KOH (1M in methanol) at 25 °C led to instantaneous formation of the hydroxycarbonyl adduct $[Ru(CO)_2Cl_2\{C(O)OH\}]^-$.[8] Decarboxylation of the latter at 100–110 °C under a stream of ethylene (1 atm) for 40 min gave **4a** in quantitative yield (by spectroscopy).[9] The reaction is easily monitored by IR spectroscopy by following the disappearance of the characteristic band of the C(O)OH group at 1527 cm^{-1}. The elusive intermediate hydrido species "$[Ru(CO)_2Cl_2H]^-$" was not detected in the presence of the olefin, and the mononuclear solvent-stabilized alkyl intermediate was observed only in dimethylformamide. Dimerization with the loss of a halide ligand is a means for the 16-electron organometallic fragment to relieve its unsaturation and to release the excess negative charge. The complex was recrystallized as its PPN salt and recovered in 60–70 % yield. This synthetic procedure is milder and faster than the original route with an alkyl formate as hydride source.[6]

The reaction sequence of Scheme 2 is applicable to a variety of other olefins;[10] hence, we were interested in its possible extension to alkynes. Thermal decarboxylation of the hydroxycarbonyl adduct at 100–110 °C for 20 min in the presence of one equivalent of diphenylacetylene gave the alkenyl complex K-**5** (Scheme 3). The complex was isolated as the PPN salt in 78 % yield. The dimeric anionic unit of [PPN]-**5** (Figure 1)[11] consists of a face-sharing bioctahedron (*gauche* isomer).



Scheme 3.

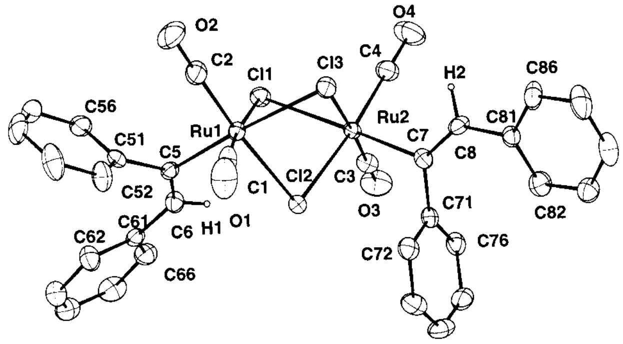
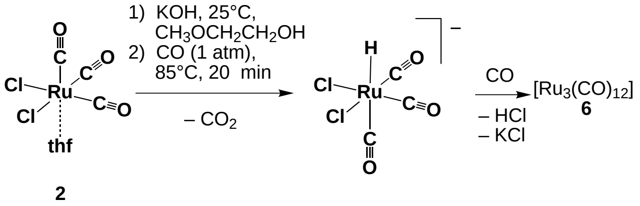


Figure 1. Perspective view of the anionic unit of the alkenyl complex [PPN]-**5**. Selected interatomic distances [Å] and angles [°]: Ru1–Ru2 3.2585(4), Ru1–Cl1 2.445(1), Ru1–Cl2 2.450(1), Ru1–C1 1.842(4), Ru1–C2 1.833(4), Ru1–C5 2.086(4), Ru2–Cl1 2.576(1), Ru2–Cl2 2.470(1), Ru2–Cl3 2.450(1), Ru2–C3 1.837(4), Ru2–C4 1.822(4), Ru2–C7 2.096(4), C5–C6 1.338(6), C7–C8 1.336(6); Ru1-C5-C6 119.1(3), Ru2-C7-C8 121.4(3).

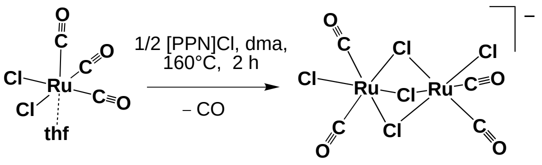
In an attempt to trap the elusive hydrido intermediate in the absence of olefinic or acetylenic substrates, we decarboxylated the hydroxycarbonyl adduct at 85 °C under a stream of carbon monoxide. This resulted in formation of $[Ru_3(CO)_{12}]$ (**6**) as orange crystals (97 % yield) on the walls of the glassware (Scheme 4). The reduction of Ru^{II} to Ru^0 can be explained in terms of the reductive elimination of HCl from an elusive hydrido species "$K[Ru(CO)_3Cl_2H]$". The acidity of the latter reflects the fact that halide ligands behave as Brønsted bases when the coordination sphere of ruthenium is saturated, which behavior was originally noted by Caulton et al. in studies on related chloro-phosphine Ru^{II} complexes.[12] The evolution of HCl gas under our experimental conditions was detected by means of an aqueous solution of $AgNO_3$ in a bubbler at the gas exit of the reflux condenser.



Scheme 4.

Due to the insolubility of $[Ru_3(CO)_{12}]$ in 2-methoxyethanol, the solution is almost colorless at the end of the reaction since it contains only KCl.[13] Significantly, this synthesis can be performed directly from commercial $RuCl_3 \cdot 3H_2O$ with almost the same efficiency in a one-pot procedure with two steps: treatment of $RuCl_3 \cdot 3H_2O$ with CO (1 atm) at 125 °C for 2 h to generate the carbonylchloro species (characteristic yellow color) and addition of KOH under CO (at 25 °C) followed by thermal decarboxylation at 85 °C under CO for 20 min. Crystals of $[Ru_3(CO)_{12}]$ (80 – 90 % yield) can then be isolated by simple filtration. In contrast, the published procedure with zinc as a halide acceptor[14] is less efficient (50 – 60 % yield), takes about 12 h, and requires further workup for separation and recrystallization.

Given the propensity of chloro-ruthenium complexes to adopt face-sharing bioctahedral structures,[12, 15] we were intrigued by the fact that the hypothetical binary carbonylchloro anion $[Ru_2(\mu\text{-}Cl)_3(CO)_4Cl_2]^-$ (**7**) has not been reported, whereas the dianionic complex $[Ru_2(\mu\text{-}Cl)_2(CO)_4Cl_4]^{2-}$ (**8**) is readily available by thermal decarbonylation of **1** or **2** in the presence of one equivalent of halide ion per ruthenium unit.[16] We have now discovered a route to **7**: it is readily prepared by thermal decarbonylation of **2** in dimethylacetamide (dma) in the presence of [PPN]Cl (Scheme 5).



2 **7** (90 %)

Scheme 5.

The X-ray structure of **7** is shown in Figure 2.[17] The complex adopts a face-sharing bioctahedral structure and is again obtained only as the *gauche* isomer, as evidenced by ^{13}C NMR data. Since the known ruthenium carbonyl-chloro species $[Ru(CO)_2Cl_2]$[5c] exists only as a polymer of undefined structure, **7** represents the simplest association of two neutral 14 e⁻ "$Ru(CO)_2Cl_2$" units slightly stabilized by one additional halide ion. With such a simple non-hydridic carbonyl-chloro Ru^{II} prototype in hand, we expected to observe the activation of terminal alkynes in the form of vinylidenes.[18] Instead, the reaction of the PPN salt of **7** with *para*-tolylacetylene (*p*-tolC≡C) in 2-methoxyethanol led exclusively to the alkyl derivative, [PPN]-**4b** (Scheme 6), which was formed in quantitative yield according to spectroscopy and recovered as an oil in 58 % yield. The cleavage of the carbon – carbon triple bond of the alkyne can be rationalized by anology to the reaction of vinylidene complexes with water.[19] The proposed reaction sequence leading to **4b** is summarized in Scheme 7.

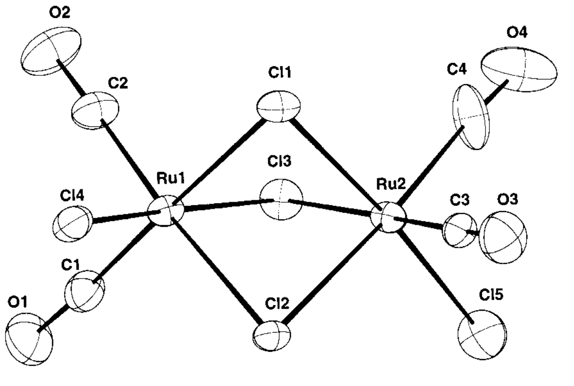
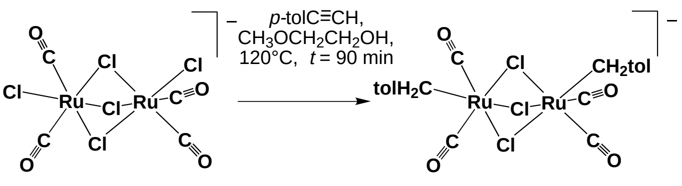
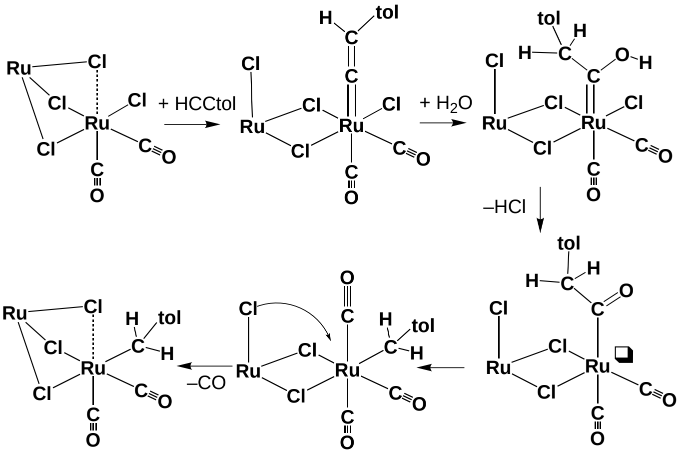


Figure 2. Perspective view of the anionic unit of the carbonyl-chloro complex [PPN]-**7**. Selected interatomic distances [Å]: Ru1–Ru2 3.1757(6), Ru1–Cl1 2.470(1), Ru1–Cl2 2.458(1), Ru1–C1 1.834(6), Ru1–C2 1.854(6), Ru1–Cl4 2.361(1), Ru2–Cl1 2.436(1), Ru2–Cl2 2.456(1), Ru2–Cl3 2.464(1), Ru2–Cl5 2.395(2), Ru2–C3 1.876(6), Ru2–C4 1.920(7).



7 **4b**

Scheme 6.



Scheme 7. Proposed reaction pathway leading to the alkyl complex **4b**. tol = *p*-tolyl. □ denotes a vacant coordination site.

The reaction of [PPN]-**7** with trimethylsilylacetylene cleanly gave the methyl derivative $[(PPh_3)_2N][Ru_2(\mu\text{-}Cl)_3(CO)_4(CH_3)_2]$ ([PPN]-**4c**),[20] obtained for the first time as pure crystals in 65 % yield and fully characterized by spectroscopic methods and X-ray diffraction.[21] Significantly, the acetylide complexes $[(PPh_3)_2N][Ru_2(\mu\text{-}Cl)_3(CO)_4(CCH)_2]$ ([PPN]-**9a**) and $[(PPh_3)_2N][Ru_2(\mu\text{-}Cl)_3(CO)_4(CCSiMe_3)_2]$ ([PPN]-**9b**; traces) were also detected (by mass spectrometry) when the reaction was carried out in the absence of water in a nonprotic solvent such as dioxane. There is a precedent for the formation of a ruthenium acetylide ([Ru]–C≡CH) on activation of trimethylsilylacetylene by a chloro ruthenium complex with concomitant elimination of $SiMe_3Cl$.[22] Here the hydration of **9a** to give **4c** probably involves an α-hydroxyvinyl intermediate $[Ru]{-}C(OH){=}CH_2$, isomerization of which into an acyl complex $[Ru]{-}C({=}O)CH_3$ followed by decarbonylation produces the methyl complex.

Thus, the facile transformations of terminal alkynes observed here can be accounted for by the existence of intermediate vinylidene complexes that are highly reactive due to the absence of electronic stabilization and steric protection of their α-carbon atom. The next challenge will be to trap such intermediates and to examine their potential applications in organic synthesis.[23]

Experimental Section

2 (optimization of published procedure):[5a] A solution of $RuCl_3 \cdot 3H_2O$ (5 g) in 2-methoxyethanol (100 mL) was treated with CO (1 atm) for 3 h at 125 °C and then for 7 h at 25 °C to give a pale yellow solution of **1**. After evaporation of the solvent (50 °C, reduced pressure), the residue was extracted with hot THF (30 mL). Complex **2** crystallized at -30 °C as white needles (4.24 g, 70% yield). IR: $\tilde{\nu} = 2115$ (vs), 2035 cm^{-1} (vs). Isolation of a second crop of crystals from the concentrated filtrate gave a total yield of **2** of 89%. The complex was identified as the *fac* isomer by X-ray diffraction.

Standard solutions of the hydroxycarbonyl adduct $K[Ru(CO)_2Cl_2\{C(O)OH\}]$ (IR: $\tilde{\nu} = 2048$ (s), 1981 (vs), 1647 (m), 1527 cm^{-1} (ms)) were prepared from **2** (500 mg, 1.52 mmol) in 2-methoxyethanol (25 mL) by adding 1.5 mL of a 1 M methanolic solution of KOH.

[PPN]-**4a**: Ethylene was bubbled into a freshly prepared solution of the hydroxycarbonyl adduct at 100–110 °C. The formation of K-**2** was complete after 40 min (spectroscopy). After addition of [PPN]Cl and evaporation of the solvent, the THF-soluble fraction was recrystallized from acetone/ethanol (1/5) at -30 °C to give [PPN]-**4a**[6] (490 mg, 65% yield). IR (CH_2Cl_2): $\tilde{\nu} = 2030$ (w,sh), 2018(vs), 1943 cm^{-1} (vs).

[PPN]-**5**: Diphenylacetylene (270 mg, 1.5 mmol) was added to a freshly prepared solution of the hydroxycarbonyl adduct, and the reaction mixture heated at 100–110 °C until the IR bands of K-**5** reached maximum intensity (ca. 20 min). Treatment with [PPN]Cl and recrystallization (acetone/ethanol) gave crystals of [PPN]-**5** $\cdot (CH_3)_2CO$ in 78% yield. IR (CH_2Cl_2): $\tilde{\nu} = 2044$ (w, sh), 2034 (vs), 1967 cm^{-1} (vs); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 6.68$–7.62 (m, vinylic and phenyl protons); MS (electrospray): m/z: 779.

6 from **2**: A freshly prepared solution of the hydroxycarbonyl adduct was heated at 85 °C under a CO stream for 20 min. After cooling, crystals of **6** were recovered by filtration and washed with ethanol (310 mg, 97% yield).

6 from $RuCl_3 \cdot 3H_2O$: A solution of $RuCl_3 \cdot 3H_2O$ (1 g, 3.82 mmol) in 2-methoxyethanol (40 mL) was heated at 125 °C under CO until a yellow color was obtained (ca. 2 h). After cooling, a methanolic solution of KOH (1 M, 4.2 mL) was added at 20 °C, and the temperature was raised to 85 °C for 20 min. Compound **6** was recovered by filtration (ca. 700 mg, 86% yield).

[PPN]-**7**: Compound **2** (1 g, 3 mmol) and [PPN]Cl (874 mg, 1.5 mmol) were dissolved in dimethylacetamide (20 mL). After heating for 2 h at 160 °C, the solvent was evaporated (90 °C, reduced pressure). The solid residue was washed with hexane. Recrystallization from dichloromethane/hexane gave [PPN]-**7** (1390 mg, 90% yield). IR (CH_2Cl_2): $\tilde{\nu} = 2068$ (vs), 2008 cm^{-1} (vs, br); ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 191.44$, 191.88 (CO); MS (electrospray): m/z: 492.6.

[PPN]-**4b**: A solution of [PPN]-**7** (1390 mg, 1.35 mmol) in 2-methoxyethanol (30 mL) and *p*-tolylacetylene (340 mg, 2.93 mmol) was heated at 110–120 °C for 90 min. After solvent evaporation (90 °C, reduced pressure), the resulting oil was washed several times with hexane and ethanol to give [PPN]-**4b** (910 mg, 58% yield). IR (2-methoxyethanol): $\tilde{\nu} = 2031$ (sh), 2019 (vs), 1948 cm^{-1} (vs, br); ^{13}C NMR (250 MHz, CD_2Cl_2): $\delta = 22.10$ (t, $CH_2C_6H_4CH_3$, $J_{C,H} = 134$ Hz), 20.87 (q, $CH_2C_6H_4CH_3$, $J_{C,H} = 126$ Hz), 126–135 (m, C_6H_4), 197.82 and 198.23 (s, CO); ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 3.46$ (s, $CH_2C_6H_4CH_3$), 2.25 (s, $CH_2C_6H_4CH_3$); MS (electrospray): m/z: 633.

[PPN]-**4c**: An analogous procedure starting from [PPN]-**7** (250 mg, 0.243 mmol) and trimethylsilylacetylene (0.067 mL, 0.485 mmol) gave crystalline [PPN]-**4c** (158 mg, 65% yield). IR (2-methoxyethanol): $\tilde{\nu} =$ 2021 (sh), 2019 (vs), 1946 cm^{-1} (vs, br) ^{13}C NMR (250 MHz, CD_2Cl_2): $\delta = -7.93$ (q, CH_3, $J_{C,H} = 134$ Hz); 126–134 (m, C_6H_5), 197.86 and 198.13 (s, CO); ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 0.84$ (s, CH_3), 7.3–7.7 (m, C_6H_5); MS (electrospray): m/z: 453.

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[8] The hydroxycarbonyl adduct can be indifferently generated in situ from any of the precursors **1**–**3** in solvents such as alcohols, THF, and DMF. In noncoordinating solvents (dichloromethane), it can dimerize by forming hydroxycarbonyl bridges. A related complex with methoxycarbonyl bridges is known.[1e]

[9] The reaction can be alternatively conducted with the same efficiency in a closed reactor under ethylene pressure (20 atm), but otherwise identical conditions.

[10] Related alkyl complexes are formed with methyl acrylate, styrene, and propylene (G. Lavigne, unpublished results).

[11] a) Crystallographic data for [PPN]-**5** $\cdot (CH_3)_2CO$: orthorhombic, space group $P2_12_12_1$, $a = 10.346(1)$, $b = 22.277(2)$, $c = 27.519(3)$ Å; $V = 6343(2)$ Å^3; $R = 0.021$, $Rw = 0.027$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-103293 ([PPN]-**5**), CCDC-103294 ([PPN]-**7**), and CCDC-112413 ([PPN]-**4c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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1433-7851/99/3804-0521 $ 17.50+.50/0

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[20] This species was originally detected in an inseparable mixture of complexes resulting from a metal-mediated degradation of methyl formate.[6]

[21] Crystal data for [PPN]-**4c**: Monoclinic, space group $P2_1/n$; $a = 29.322(4)$, $b = 15.558(2)$, $c = 9.656(2)$ Å, $\beta = 92.77(2)$, $V = 4400(2)$ Å^3; $R = 0.046$, $Rw = 0.050$.[11b]

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[23] Carbenoid species derived from simple carbonyl-chloro Ru^{II} complexes have been recently proposed by Murai et al. as intermediates in the construction of polycyclic ring systems from enynes.[4a]

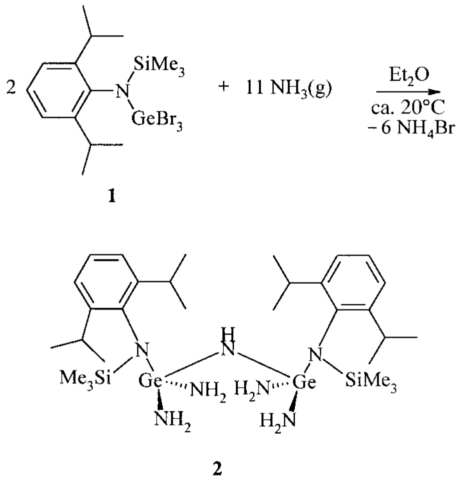
Reaction of $RGeBr_3$ ($R = i Pr_2C_6H_3NSiMe_3$) with Ammonia To Give $(RGe)_2(NH_2)_4(NH)$: A Compound Containing Terminal NH_2 Groups[**]

Karsten Wraage, Lutz Lameyer, Dietmar Stalke, and Herbert W. Roesky[*]

In memory of Jean Rouxel

In the past few years Power et al.,[1] Schnick et al.,[2] and others[3, 4] have shown that amino and imino derivatives containing silicon can undergo interesting reactions. In this respect they resemble the oxygen derivatives to some extent, but they can also differ from them quite considerably.[5] For example, $RSi(NH_2)_3$ compounds react with $AlMe_3$ and $[Cp^*TiMe_3]$ ($Cp^* = C_5Me_5$) with elimination of methane to form interesting, new, soluble heterocycles. We were interested in finding out whether there is a similar successive chemistry for germanium derivatives. We quickly discovered that the preferred starting compound for the reaction with ammonia—namely, $RGeCl_3$ ($R = i Pr_2C_6H_3NSiMe_3$)—is not accessible in a pure form. Until now, only one monoaminogermanium compound with the composition Mes_3GeNH_2 ($Mes = Me_3C_6H_2$) was known which is stable with regard to condensation reactions.[6] We report here on the preparation and structure of an amino-iminogermanium compound with free amino groups that have not undergone condensation reactions.

To obtain a suitable reagent for the synthesis of an amino derivative, we first prepared tribromogermanium compounds of the type $RGeBr_3$. The compound $i Pr_2C_6H_3NSiMe_3GeBr_3$ (**1**) was obtained by reaction of $i Pr_2C_6H_3NSiMe_3Li$ with $GeBr_4$ in diethyl ether at −78 °C under elimination of LiBr. The reaction of **1** in liquid ammonia, which was performed analogous to the synthesis of $RSi(NH_2)_3$ derivatives,[1, 3] proved to be unsuccessful; due to condensation reactions no definitive product could be isolated. If **1** is dissolved at room temperature in diethyl ether and ammonia is passed through the reaction solution, however, $(RGe)_2(NH_2)_4(NH)$ (**2**) is obtained in good yield (Scheme 1).



Scheme 1. Synthesis of **2** from **1**.

Compound **2** was studied by NMR spectroscopy, mass spectrometry, and structure analysis. In the ^1H NMR spectrum the characteristic signals for the NH and NH_2 protons are recognizable as broad singlets ($\delta = 0.65$ for $(RGe)_2(NH_2)_4(N\mathit{H})$ and $\delta = 0.75$ for $(RGe)_2(N\mathit{H}_2)_4NH$). The IR spectrum shows three N–H bands in the bond stretching region (3325–3402 cm^{-1}), and the bands at 1540 and 1578 cm^{-1} have been provisionally assigned to the NH_2 bending vibrations.

Single crystals of **2** are obtained on recrystallization from *n*-hexane. Compound **2** crystallizes in the space group $P\bar{1}$;[11] two $RGe(NH_2)_2$ fragments bridged by a NH group are shown in the asymmetric unit in Figure 1 a. In spite of their comparatively large spatial requirement, both of the *N*-(2,6-diisopropylphenyl)-*N*-(trimethylsilyl)amino groups are located on one side of the molecule and the four NH_2 groups on the opposite side. This cisoid arrangement is the result of a network of bridging hydrogen bonds (Figure 1 b). The centrosymmetric dimer has four weak N ··· H-N bridges.[7] The N ··· H distances are 250.5 pm (H21 ··· N5A, H21A ··· N5; Figure 1 b) and 267.8 pm (H31 ··· N2A, H31A ··· N2; Figure 1 b). All the Ge–N bond lengths to the hydrogen-substituted nitrogen atoms N1, N2, N3, N5, and N6 lie in the range from 181.1(2) to 182.4(2) pm, the bonds to the aryl-substituted nitrogen atoms N4 and N7 (both 184.2(2) pm) are about 3 pm longer.

The Ge–N bond lengths all lie in the expected region. Similar derivatives, such as the NH-bridged compound $[Me_2Si(N t Bu)_2Ge(t Bu)]NH[(C_5H_4N)Ge(N t Bu)_2SiMe_2]$ described by Veith et al. and the cyclotris(dithiolato)germanium imide $[\{(t BuS)_2Ge(NH)\}_3]$ described by George et al., have

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