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Communications

Dehydrohalogenation by a Germylene: Conversion of Carbene Ligands into Carbynes at Ruthenium

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Summary: The dialkylgermylene [Ge(CH[SiMe$_3$]$_2$)$_2$] (**3**) *converts the carbene complexes* [Ru(CHR)(PCy$_3$)$_2$Cl$_2$] (*R* = *p*-C$_6$H$_4$Me [**2**], *n*-C$_4$H$_9$ [**6**]) *into the corresponding square-planar carbyne complexes* [Ru(CR)(PCy$_3$)$_2$Cl] (*R* = *p*-C$_6$H$_4$Me [**1**], *n*-C$_4$H$_9$ [**7**]) *cleanly within minutes at 25 °C in benzene; addition of HCl to a benzene solution of* **1** *results in quantitative re-formation of* **2**. *Replacement of chloride in* **1** *affords other halide and pseudohalide complexes,* [Ru(C-*p*-C$_6$H$_4$Me)(PCy$_3$)$_2$X] (*X* = *p*-OC$_6$H$_4$-*t*-Bu, Br, F, O$_3$SCF$_3$), *cleanly.*

Transition-metal complexes that contain the carbyne moiety have received considerable attention of late for their bonding properties as well as their growing application in organic and materials synthesis, especially alkyne metathesis.[1,2] Since Fischer reported the first transition-metal carbyne complexes in 1973, a variety of synthetic routes to compounds that contain a metal−carbon triple bond have been developed.[1,3−6]

Notwithstanding the existence of several terminal ruthenium−carbyne complexes,[3,7−11] homogeneous alkyne metathesis catalysis remains restricted to complexes of Mo, W, and Re.[1] In an effort directed toward the discovery of late-metal carbyne complexes that can mediate acetylene metathesis, we sought a general means of obtaining carbyne complexes directly from the multitude of carbene complexes that have been developed for olefin metathesis.[12]

Recently, Caulton disclosed the unanticipated formation of the square-planar Ru−carbyne complexes [Ru(CPh)(OPh)(PR$_3$)$_2$] (R = *i*-Pr, Cy) by treatment of [Ru(CHPh)(PR$_3$)$_2$Cl$_2$] with excess NaOPh.[7] The product selectivity appears to be driven by steric interactions at an intermediate stage.[13] In some cases, four-coordinate carbene complexes of the form [Ru(CHPh)(PR$_3$)(OR)$_2$] are formed instead by loss of phosphine rather than alcohol.[7,8] We report herein rapid and reliable syntheses of a family of Ru−carbyne complexes of the form [Ru(CR)(PCy$_3$)$_2$X] (R = alkyl, aryl; X = Cl, F, Br, *p*-OC$_6$H$_4$C-*t*-Bu). The parent compound in this series, [Ru(C-*p*-C$_6$H$_4$Me)(PCy$_3$)$_2$Cl] (**1**), is formed rapidly upon treatment of the Grubbs-type olefin metathesis catalyst [Ru(CH-*p*-C$_6$H$_4$Me)(PCy$_3$)$_2$Cl$_2$] (**2**)[14] with a bulky dialkylgermylene, [Ge(CH[SiMe$_3$]$_2$)$_2$] (**3**).[15] Subsequently, the other complexes in the series are readily prepared by substitution of the chloride in **1** (Scheme 1). For synthesis of **1** on a multigram scale, a two-step process involving the synthesis of the aryloxide complex [Ru(C-*p*-C$_6$H$_4$Me)(OC$_6$H$_4$-*p*-*t*-Bu)(PCy$_3$)$_2$] (**4**), followed by its conversion into **1** using SnCl$_2$, is more economical. Compound **3** has been used recently to achieve C−H activation of alkanes, ethers, and ketones;[16,17] under some conditions, net HCl addition to **3** occurs, yielding [GeHCl(CH[SiMe$_3$]$_2$)$_2$] (**5**).

The dehydrochlorination reaction proceeds smoothly to completion over the course of 20 min under typical conditions. The expected germanium byproduct, **5**, was identified in the reaction mixture by its ^{1}H NMR spectrum but was not isolated.[17] Following removal of volatile materials in vacuo, blue-green **1** was obtained in 41.5% yield upon rinsing the solid residue with hexanes. The presence of β-H atoms on the carbene moiety does not interfere with the reaction: [Ru(CH-*n*-Bu)(PCy$_3$)$_2$Cl$_2$] (**6**)[14] undergoes similarly rapid conversion to [Ru(C-*n*-Bu)(PCy$_3$)$_2$Cl] (**7**) upon treatment with **3**. In contrast, the parent methylidyne complex [Ru(CH)-

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(1) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vols. 1−3.

(2) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605.

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

(4) Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH: New York, 1988.

(5) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281.

(6) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.

(7) Coalter, J. N.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 925.

(8) Sanford, M. S.; Henling, L. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3451.

(9) Gonzalez-Herrero, P.; Weberndorfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3266.

(10) Gonzalez-Herrero, P.; Weberndorfer, B.; Ilg, K.; Wolf, J.; Werner, H. *Organometallics* **2001**, *20*, 3672.

(11) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757.

(12) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(13) Conrad, J. C.; Amoroso, D.; Czechura, P.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2003**, *22*, 3634.

(14) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

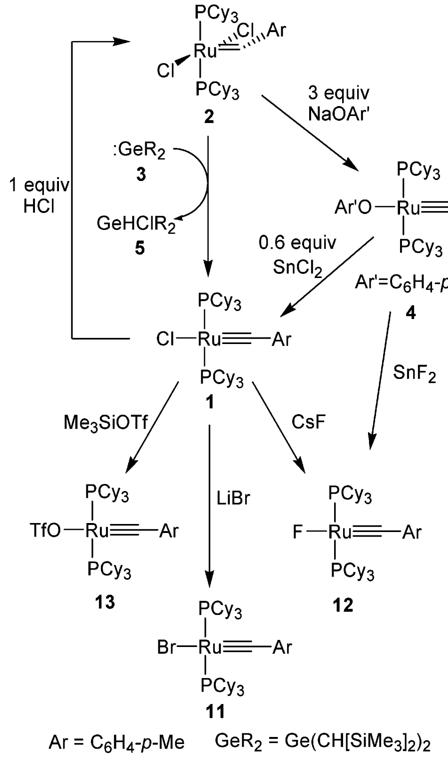
(15) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(16) Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Holl, M. M. B.; Wells, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 8986.

(17) Sweeder, R. D.; Miller, K. A.; Edwards, F. A.; Wang, J.; Holl, M. M. B.; Kampf, J. W. *Organometallics* **2003**, *22*, 5054.

10.1021/om0508482 CCC: $30.25

Scheme 1. Syntheses and Reactions of 1



$(PCy_3)_2Cl]$ could not be prepared from $[Ru(CH_2)(PCy_3)_2Cl_2]$ (**8**)[14,18] in this manner. Instead, **8** underwent slow decomposition without formation of **5**. The lack of reactivity of **8** compared to that of **2** and **6** may be due to the substantially slower rate of phosphine dissociation from the former compared to the latter complexes.[19] We note that added phosphine retards the conversion of **2** and **6** into **1** and **7**. Initial phosphine dissociation is consistent also with the observation by ^{31}P NMR spectroscopy of rapid formation of a small quantity of free PCy_3 that persists throughout reactions of **2** and **6**, but not of **8**, with **3**. Interestingly, unlike **3**, the amidogermylene $[Ge(N[SiMe_3]_2)_2]$ (**9**) fails to convert **2** into **1** in appreciable yield. The related dialkylstannylene $[Sn(CH[SiMe_3]_2)_2]$ (**10**)[15] also reacts with **2**, although other products are also formed, as the **1** produced in the reaction reacts further with additional **10**. Thus, in the reaction of **2** with 3 equiv of **10**, free PCy_3 is the only phosphorus-containing species observable by ^{31}P NMR spectroscopy after 40 min. When **2** reacts with just 1 equiv of **10** overnight, the resulting mixture contains unreacted **2**, **1**, and free PCy_3 in a 54:15:31 integration ratio. Addition of 2 equiv of **10** to a solution of **1** yields primarily free PCy_3 after 3 h, as well as minor new signals at δ 97.8 and 69.9 in the ^{31}P NMR spectrum; these species as well as any other Ru-containing products have not yet been characterized.

Complex **1** is a versatile starting material for the synthesis of other square-planar carbyne complexes, upon substitution of the chloride ligand. Upon treatment of **1** in 4:1 toluene:THF with a 10-fold excess of LiBr, $[Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2Br]$ (**11**) is formed rapidly and may be isolated in 71% yield. Several reagents effect the transformation of **1** into $[Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2F]$ (**12**). Reaction of **1** with excess CsF in THF is slow, proceeding to the extent of only 50% over 2 weeks at room temperature; the rate of conversion is enhanced by addition of 18-crown-6. Similarly, SnF_2 in THF gives slow conversion to **12**. More rapid is the reaction of **1** with $[S(NMe_2)_3][SiF_2Me_3]$ in THF. When excess CsF is used in 3:2 DME/THF containing 1.2 equiv of 18-crown-6, **12** is formed quantitatively over 48 h and can be isolated in 40% yield after two recrystallizations. In THF, **12** exhibits a distinctive doublet in the ^{31}P NMR spectrum at δ 47.1 ($^2J_{FP}$ = 37 Hz) due to coupling to one F ligand; the ^{19}F NMR spectrum shows a triplet at δ −191.1 with the same coupling constant, indicating the presence of two equivalent P nuclei. Treatment of a blue-green solution of **1** in C_6D_6 with Me_3SiOTf (Tf = CF_3SO_2) causes precipitation of a blue-green powder that analyzes as $[Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2OTf]$ (**13**). Dissolution of this compound in THF gives rise to a blue-green solution that exhibits single peaks at δ 44.0 in the ^{31}P NMR spectrum and δ −77.5 in the ^{19}F NMR spectrum. This complex is unstable in THF and pyridine, undergoing conversion to uncharacterized products. Addition of NaOAr (Ar = $p\text{-}C_6H_4\text{-}t\text{-}Bu$) to **1** results in clean conversion to **4**, which is isolated in 59% yield. The reverse transformation is best accomplished by addition of **4** dissolved in THF to 0.6 equiv of $SnCl_2$ also in THF, resulting in an 87% isolated yield of **1**. The order of addition is important to avoid formation of a significant amount of an uncharacterized dark purple contaminant. Complex **4** can also be prepared directly from **2** in 66% isolated yield by treatment with 3 equiv of NaOAr in 4:1 toluene/THF.

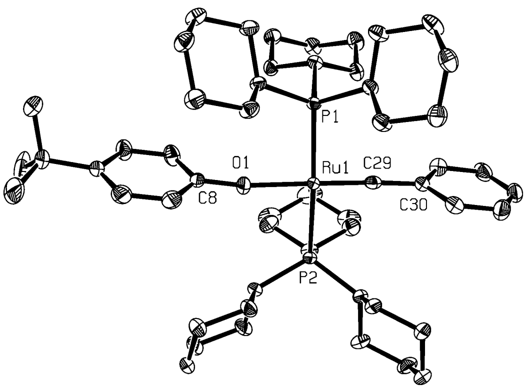


Figure 1. Thermal ellipsoid plot of **14**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru1−C29, 1.7178(16); Ru1−O1, 1.9938(13); Ru1−P1, 2.3875(7); Ru1−P2, 2.3964(7); Ru1−C29−C30, 176.40(14); Ru1−O1−C8, 170.83(12); C29−Ru1−O1, 176.42(7); C29−Ru1−P1, 91.63(6); O1−Ru1−P1, 90.36(4); C29−Ru1−P2, 90.09(6); O1−Ru1−P2, 87.67(4); P1−Ru1−P2, 174.838(16).

Unlike the prototypical *trans*-$[Ru(CPh)(OPh)(P\text{-}i\text{-}Pr_3)_2]$,[7] closely related $[Ru(CPh)(O\text{-}p\text{-}C_6H_4\text{-}t\text{-}Bu)(PCy_3)_2]$ (**14**) does not suffer from disorder of the benzylidyne and phenoxide ligands in the single-crystal X-ray structure. Complex **14** crystallized in the space group $P2_1/c$, with one molecule of **14** and 0.5 disordered Et_2O molecules in the asymmetric unit. A thermal ellipsoid plot of **14** is depicted in Figure 1, along with selected bond lengths and angles. The complex adopts a square-planar geometry in the solid state, with bond angles about Ru in

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[18] Pietraszuk, C.; Marciniec, B.; Fischer, H. *Organometallics* **2000**, *19*, 913.

[19] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.

the range 87.67(4)−91.63(6)° (angle sum 359.75°). The Ru≡C bond length of 1.7178(16) Å is significantly longer than the corresponding bond length of 1.660(5) Å found in the square-pyramidal cation $[Ru(CCH_2Ph)(P\text{-}i\text{-}Pr_3)_2Cl_2]^+$ [10] but shorter than the Ru=C internuclear separation of 1.839(3) Å in the Grubbs-type carbene complex $[Ru(CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2Cl_2]$.[14]

In summary, dehydrohalogenation of the Ru-based olefin metathesis catalysts **2** and **6** by the dialkylgermylene **3** effects their conversion into carbyne complexes. Halide substitution in the latter complexes is facile, affording access to other halide and pseudohalide complexes. These include fluoro complex **12** as well as aryloxide complex **14**, which is square planar in the solid state. We are currently investigating the utility of these carbyne complexes in the synthesis of hitherto unavailable carbene complexes, as well as their conversion into complexes that may be active in alkyne metathesis. We are also examining the scope of the dehydrohalogenation reaction of late-metal carbene complexes by germylene **3**.

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Supporting Information Available: Text giving all synthetic procedures and analytical data for new compounds and a CIF file giving single-crystal X-ray diffraction data for **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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