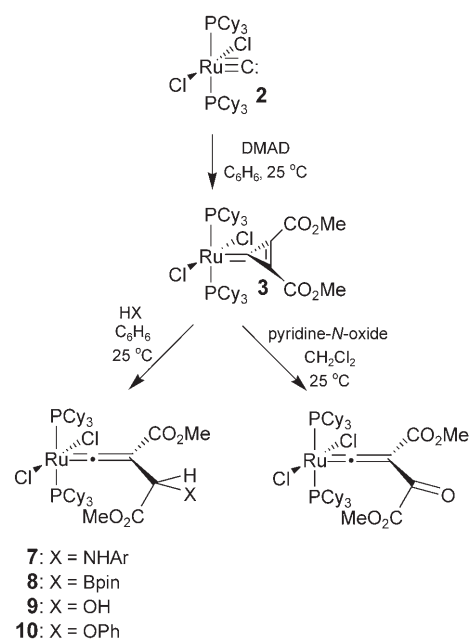


Carbon–Carbon Bond Formation at a Neutral Terminal Carbido Ligand: Generation of Cyclopropenyldiene and Vinylidene Complexes**

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Olefin metathesis is an important tool for organic and polymer synthesis.^[1] However, some key functional groups are not tolerated even by Ru-based catalysts.^[2] We recently showed that vinyl esters can deactivate [Ru(CHPh)(PCy₃)₂Cl₂] (**1**)^[3] by quantitative formation of [Ru(C)(PCy₃)₂Cl₂] (**2**)^[4,5] A rare neutral terminal carbido complex,^[4–7] **2** is surprisingly stable and has few reported reactions.^[5–7] However, protonation of **2** by strong acid yields catalysts that rapidly initiate olefin metathesis.^[7] Thus, **2** is both a precursor to and a decomposition product of olefin metathesis catalysts. We see **2** as a potential source of a C₁ fragment. Accordingly, we describe herein the first C–C bond-forming reaction of this unusual compound.

The terminal carbido ligand in **2** is a poor nucleophile, as shown by its failure to react with MeI, MeCOCl, and PhCH₂Br. Although **2** does not react with a variety of alkenes and alkynes (see the Supporting Information), it reacts cleanly with MeO₂CC≡CCO₂Me (dimethyl acetylenedicarboxylate, DMAD) over 4 h in C₆H₆. A new blue-purple complex, **3**, is formed as the carbido signal for **2** (¹³C NMR: δ = 471.8 ppm) is replaced by a new signal at δ = 195.7 ppm. The ¹H NMR spectrum evinces formation of a 1:1 adduct of **2** with DMAD. Formation of the cyclopropenyldiene complex [Ru{=CC₂(CO₂Me)₂}(PCy₃)₂Cl₂] (Scheme 1) accounts for these observations. Several cyclopropenyldiene complexes exist. Unlike **3**, however, the cyclopropenyldiene units in these complexes are substituted by phenyl or electron-donating groups.^[8–23] [Ru(C)(H₂IMes)(PCy₃)Cl₂] (**4**; H₂IMes = 4,5-dihydro-1,3-bis(mesityl)imidazol-2-ylidene) reacts similarly with DMAD, but the reaction is not clean since the product reacts further with DMAD before all of **4**



Scheme 1. Formation of **3** and ring-opening reactions. HBpin = pinacolborane, Ar = 3,5-Me₂C₆H₃.

has been consumed. However, **4** reacts more cleanly with HC≡CCO₂Me (see the Supporting Information).

Single-crystal X-ray diffraction confirmed the structure of **3**.^[24] Figure 1 depicts a thermal ellipsoid plot of one of the two chemically equivalent but crystallographically independent molecules of **3** in the crystal. The data establish the expected connectivity in **3**, but the large uncertainty associated with the Ru=C bond length of 1.846(10) Å precludes comparison with those in related alkylidene complexes. The cyclopropenyldiene ring lies in the Cl–Ru–Cl plane. The structure shows significant bond localization in the cyclopropenyldiene fragment. These distances closely resemble those observed in free

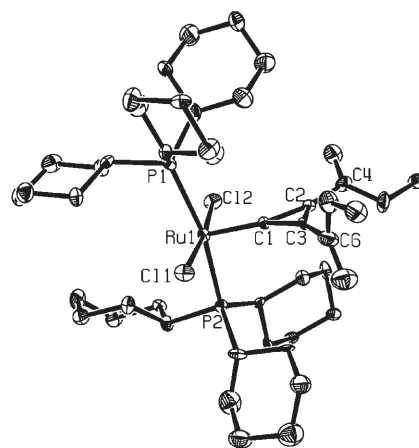


Figure 1. X-ray crystal structure of **3** (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ru1–C1 1.846(10), Ru1–Cl1 2.389(3), Ru1–Cl2 2.402(3), Ru1–P1 2.407(3), Ru1–P2 2.390(3), C1–C2 1.410(13), C1–C3 1.425(14), C2–C3 1.300(14); C1–Ru1–Cl1 91.6(3); C1–Ru1–Cl2, 95.3(3), C1–Ru1–P1 97.0(3), C1–Ru1–P2 95.8(3), C2–C1–C3 54.6(7), C1–C2–C3 63.3(7), C1–C3–C2 62.1(7).

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$C_3(NiPr_2)_2$ (**5**)^[25] and in other cyclopropenylidene complexes.^[9,14–23]

The formation of **3** from **2** is interesting because the cyclopropylidene complex $[Ru(=CC_2H_2(CO_2Me)_2)(PCy_3)_2Cl_2]$ (**6**) is not observed as an intermediate when **2** is formed from **1** by reaction with Feist's ester.^[4] Addition of 2 equivalents or less of PCy_3 to $[Ru(=CC_2H_2(CO_2Me)_2)(PPh_3)_2Cl_2]$ similarly yields **2**. In this case, too, **6** is not seen.^[6]

The ^{13}C NMR shifts of the ring atoms in **3**, 195.7 and 162.2 ppm, closely resemble those observed for **5**^[25] but less so other cyclopropenylidene complexes, for which some cyclopropenium character is often invoked.^[14–23] Unlike **1**, **3** does not react appreciably with common olefins or alkynes, although under some conditions small amounts of **2** are formed, suggesting reversibility of the **2**→**3** transformation (see the Supporting Information). However, several reagents effect 1,1-addition of HX to the ring to form vinylidene complexes **7**–**10**; reaction with pyridine-*N*-oxide similarly yields **11** (Scheme 1). Cyclopropenium character could account for the observed reactivity, as all the reagents shown can act first as nucleophiles; however, there may be other explanations.

The structure of one vinylidene complex, $[Ru(=C(CO_2Me)CH(NHAr)CO_2Me)(PCy_3)_2Cl_2]$ (**7**, Ar = 3,5-Me₂C₆H₃), was determined by single-crystal X-ray diffraction.^[26] The vinylidene unit is apical in square-pyramidal **7** (Figure 2).

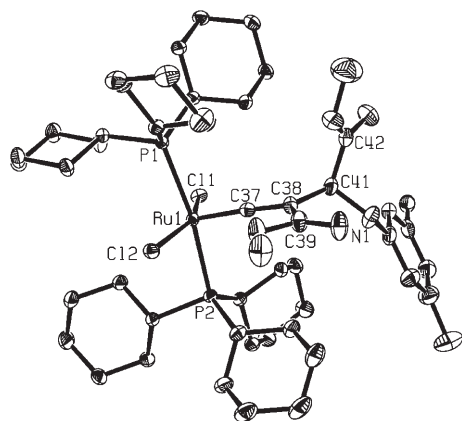


Figure 2. X-ray crystal structure of **7** (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ru1–C37 1.7458(17), Ru1–Cl1 2.3441(4), Ru1–Cl2 2.3454(4), Ru1–P1 2.4405(4), Ru1–P2 2.4098(4), C37–C38 1.344(2); C37–Ru1–Cl1 105.16(5), C37–Ru1–Cl2 100.68(5), C37–Ru1–P1 95.78(5), C37–Ru1–P2 93.39(5), Ru1–C37–C38 176.16(14), C37–C38–C39 118.76(16), C37–C38–C41 121.94(16), C39–C38–C41 119.23(15).

Ruthenium vinylidenes are useful as catalysts and catalyst precursors for olefin metathesis, alkyne dimerization, and other reactions.^[27,28] Like the “parent” vinylidene complex $[Ru(=C=CH_2)(PCy_3)_2Cl_2]$,^[3] **7**–**11** do not catalyze the ring-closing metathesis of diethyl diallylmalonate, but they do polymerize norbornene.

In summary, terminal carbido complex **2** undergoes [2+1] addition with DMAD to yield the cyclopropenylidene complex **3**. Complex **4** reacts similarly with $HC=CCO_2Me$ in

the first C–C bond-forming reactions reported for neutral terminal carbido complexes. Protic reagents HX (X = OH, OPh, $NH(3,5-Me_2)C_6H_3$) as well as pinacolborane add in a 1,1 manner to one of the distal ring C atoms in **3**, forming vinylidene complexes **7**–**11** in high yield. We are currently exploring the reactivity of **7**–**11** as well as seeking a means of regenerating a metathesis-active alkylidene complex or the carbide complexes **2** and **4**.

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tions, 8524 unique ($R_{\text{int}}=0.1875$), 4942 reflections with $I_{\text{net}} > 2.0(I_{\text{net}})$, $\mu=0.681 \text{ mm}^{-1}$, min/max transmission = 0.8758 and 0.9412, $R1$ ($I > 2\sigma$) = 0.0775, $wR2=0.1954$, GoF = 1.066, no. of parameters = 1056, final difference map within 1.008 and $-1.258 \text{ e } \text{\AA}^{-3}$. CCDC-604841 (**3**·1.5 CH₂Cl₂) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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