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: \( \delta = 471.8 \) ppm) is replaced by a new signal at \( \delta = 195.7 \) ppm. The 1H NMR spectrum evinces formation of a 1:1 adduct of 2 with DMAD. Formation of the cyclopropenylidene complex [Ru(=C=CCO2Me)](PCy3)2Cl2 (Scheme 1) accounts for these observations. Several cyclopropenylidene complexes exist. Unlike 3, however, the cyclopropenylidene 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 has been consumed. However, 4 reacts more cleanly with HCC=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 cyclopropenylidene ring lies in the Cl-Ru-C1 plane. The structure shows significant bond localization in the cyclopropenylidene fragment. These distances closely resemble those observed in free

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

**Figure 1.** X-ray crystal structure of 3 (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ru1-C1 1.846(10), Ru1-C11 2.389(3), Ru1-C12 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-C11 91.6(3); C1-Ru1-C12, 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).
C₃(ΝPr)₂ (5)[25] and in other cyclopentenyldiene complexes.[19,14–23]

The formation of 3 from 2 is interesting because the cyclopentylene complex [Ru(=CC₅H₅)(CO₂Me)₂(PCy₃)₂Cl₂] (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 PCy₃ to [Ru(=CC₅H₅)(CO₂Me)₂(PCy₃)Cl₂] similarly yields 2. In this case, too, 6 is not seen.[26]

The ¹³C 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 cyclopentenyldiene complexes, for which some cyclopentenium 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). Cyclopentenium 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≡C-C(=CH₂)N(3,5-Me₂)C₆H₃)CO₂Me(CO₂Me)PCy₃]₂Cl₂ (7, Ar = 3,5-Me₂C₆H₅), was determined by single-crystal X-ray diffraction.[24] 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-C11 2.3441(4), Ru1-C12 2.3454(4), Ru1-P1 2.4405(4), Ru1-P2 2.4098(4), C37-C38 1.344(2), C37-Ru1-C11 105.16(5), C37-Ru1-C12 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).](Image 86 to 257)

Ruthenium vinylidenes are useful as catalysts and catalyst precursors for olefin metathesis, alkylene dimerization, and other reactions.[17,26] Like the "parent" vinylidene complex [Ru(C≡C=CH₂)(PCy₃)₂Cl₂],[17] 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 cyclopentenyldiene complex 3. Complex 4 reacts similarly with HC=CO₂Me in the first C–C bond-forming reactions reported for neutral terminal carbido complexes. Protic reagents HX (X = OH, OPh, NH(3,5-Me₂)C₆H₅) 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.

Keywords: carbides · cycloaddition · cyclopentenyldiene ligands · ruthenium · vinylidene ligands

[24] Crystal data for 3·1.5CH₂Cl₂: C₃H₅Ru₂P₂O₄Cl₂, monoclinic, P2₁/c, a = 11.926(2), b = 18.555(3), c = 45.638(8) Å, β = 96.800(3)°, V = 10208(3) Å³, Z = 8, μ(MoKα) = 1.344 g cm⁻³, MoKα radiation, λ = 0.71073 Å, θ = 123(2) K, 43778 measured reflections.
tions, 8524 unique \((R_{int} = 0.1875)\), 4942 reflections with \(I_{net} > 2.0 (I_{net})\), \(\mu = 0.681 \text{ mm}^{-1}\), min/max transmission = 0.8758 and 0.9412, \(R_1 (I > 2\sigma) = 0.0775\), \(wR_2 = 0.1954\), GoF = 1.066, no. of parameters = 1056, final difference map within 1.008 and \(-1.258\) e\(\text{Å}^{-3}\), CCDC-604841 \((3\cdot1.5\text{CH}_2\text{Cl})\) 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.


[26] Crystal data for 7: \(\text{C}_{51}\text{H}_{83}\text{Cl}_{2}\text{NO}_{4}\text{P}_{2}\text{Ru}\), monoclinic, \(P2_1/c\), \(a = 15.5355(8)\), \(b = 18.9133(10)\), \(c = 17.5169(9)\) Å, \(\beta = 97.403(1)^\circ\), \(V = 5104.0(5)\) Å\(^3\), \(Z = 4\), \(\rho_{calc} = 1.312 \text{ g cm}^{-3}\). Mo\(_{Ka}\) radiation, \(\lambda = 0.71073\) Å, \(T = 123(2)\) K, 101108 measured reflections, 12702 unique \((R_{int} = 0.0321)\), 11419 reflections with \(I_{net} > 2.0 (I_{net})\), \(\mu = 0.518 \text{ mm}^{-1}\), min/max transmission = 0.8197 and 0.8602, \(R_1 (I > 2\sigma) = 0.0295\), \(wR_2 = 0.0740\), GoF = 1.059, no. of parameters = 554, final difference map within 0.885 and \(-0.727\) e\(\text{Å}^{-3}\), CCDC-604842 \((7)\) contains the supplementary crystallographic data for this paper. Data can be obtained as in Reference [24].
