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The Metathesis-Facilitated Synthesis of Terminal Ruthenium Carbide Complexes: A Unique Carbon Atom Transfer Reaction

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Despite the recognized importance of carbides as intermediates in the initial dissociation of carbon monoxide on transition metal surfaces in Fischer−Tropsch processes, few transition metal complexes containing terminal carbido ligands are known.[1,2] Anionic molybdenum and tungsten carbides, recently prepared through the deprotonation of methylidyne functional groups, remain the only examples of transition metals coordinated to a terminal carbon atom.[3−5] Carbide intermediates formed through the cleavage of CO by transition metal complexes are known to form structurally diverse polynuclear carbide-bridged compounds.[6−11] Only complexes that possess a relatively inert and congested coordination sphere appear to protect terminal carbide functionality. We report the discovery of a new class of air-stable terminal ruthenium carbide complexes prepared by a novel metathesis-facilitated reaction.

During the investigation of a new class of ruthenium-mediated ring expansion reactions,[12] we performed a stoichiometric reaction between Grubbs' ruthenium benzylidene catalysts (**1** and **2**)[13,14] and *trans*-2,3-dicarbomethoxymethylenecyclopropane (Scheme 1).[15]

Recrystallization of the ruthenium-containing product derived from **1** in chloroform produced large air-stable yellow crystals that analyzed as $Ru(C)Cl_2(P(C_6H_{11})_3)_2{\cdot}(CHCl_3)_2$ (**3**) in 54% yield. Carbide **3** is diamagnetic, air-stable, and soluble in dichloromethane and sparingly soluble in pentane. NMR spectra of the complex show both the absence of a methylidyne peak in the ^1H NMR and a quaternary ^{13}C resonance at $\delta = 471.5$, similar to the terminal carbide resonances observed in the previously reported molybdenum and tungsten complexes.[4,5] An isostructural product, **4**, in which one of the tricyclohexylphosphine ligands is replaced by a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand was isolated from a reaction between **2** and the methylenecyclopropane precursor in 20% yield. Styrene and dimethyl fumarate products were identified in NMR and GC/MS spectra of crude reaction residues.

Yellow crystals of **4** were subjected to X-ray crystallographic analysis and a representation of the resulting structure is shown in Figure 1.[16,17] The distorted trigonal bipyramidal coordination environment around the ruthenium atom surrounds the terminal carbide unit with two adjacent cyclohexyl groups and one of the mesityl units. A molecule of benzene is included in a cleft formed by the proximal cyclohexyl and mesityl ligands. The Ru−C distance of 1.650 (2) Å is among the shortest distances observed for Ru−C triple bonds.[18,19] This distance is 0.15 Å shorter than typical Ru−C distances in alkylidene complexes.[13,20,21] The Ru−P and Ru−Cl distances are virtually identical to analogous bonds in ruthenium alkylidene complexes. This seems to suggest substantial similarity in the electronic environment at ruthenium among the alkylidene and carbide complexes.

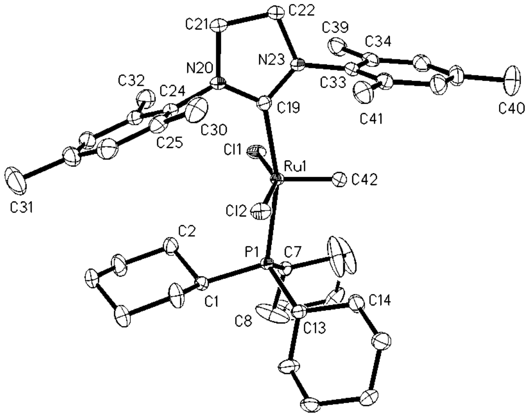
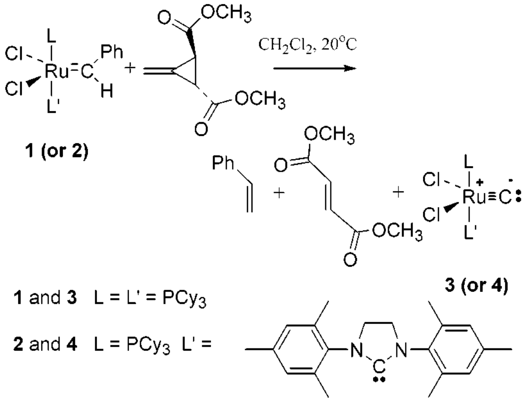
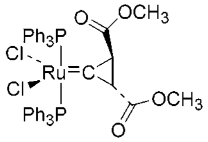


Figure 1. X-ray structure of $Ru(C)Cl_2(P(cyclohexyl)_3)-(1,3\text{-dimesityl-}4,5\text{-dihydroimidazol-2-ylidene}){\cdot}C_6H_6$.

Scheme 1



Grubbs has reported the isolation of **5** from reactions between *trans*-2,3-dicarbomethoxymethylenecyclopropane and $Ru(CH-CHC(C_6H_5)_2)Cl_2(P(C_6H_5)_3)_2$, a bis-triphenylphosphine-substituted analogue of compounds **1** and **2**.[22] An isostructural bis-tricyclohexylphosphine analogue of **5** is a likely intermediate in the formation of **3**. The relative stability of **5** may be due to the poorer electron-donating ability of the triphenyl phosphine ligands. Electron density from the ruthenium center may be required to stabilize the developing triple bond to the carbide unit during the unusual elimination of the dimethylfumarate product (Scheme 2).



5

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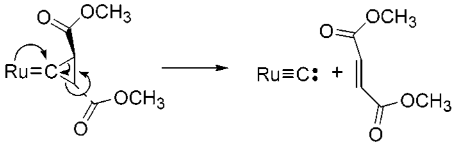
Scheme 2



We are currently investigating whether the mechanism of the elimination reaction is a stepwise or concerted process and studying the chemical reactivity of the carbide functional group.

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Supporting Information Available: Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Synthesis of (**3**): Under argon, 0.0227 g (1.334×10^{-4} moles) of *trans*-2,3-dicarbomethoxymethylenecyclopropane was dissolved in 5 mL of dry dichloromethane. This was added to 0.0450 g (5.468×10^{-5} moles) of **1** in 25 mL of dichloromethane. The solution changed from deep purple to brown/pink. The solvent was removed in vacuo to give a brown/pink powder. This was repeatedly washed with cold pentane to give a pale powder in 54% yield. Yellow crystals were obtained by recrystallization from chloroform. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.59 (m, 6H), 2.15 (pseudo doublet, 12H), 1.85 (m, 12H), 1.74 (broad singlet, 6H), 1.62 (pseudo quartet, 12 H), 1.26 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, 64 000 scans, δ): 471.8 (s), 31.97 (t), 30.08 (s), 28.10 (t), 26.87, (s). ^{31}P (500 MHz, $CDCl_3$, δ): 38.3 (s). FAB-MS (NBA matrix): *m/z* [isotope cluster consistent with the primary species $M + H^+$] calcd for $C_{37}H_{67}Cl_2P_2Ru$, 745.85; found, 745.4. Anal. Calcd for $C_{37}H_{66}Cl_2P_2Ru$: C, 59.66; H, 8.93. Found: C, 59.93; H, 8.69.

(16) Using the same procedure as for (**3**), 0.0949 g (1.118×10^{-4} mol) of **2** reacted with 0.1257 g (8.721×10^{-4} mol) of *trans*-2,3-dicarbomethoxymethylenecyclopropane. The initial brown/purple solution changed to a brown solution. The brown product was dissolved in pentane, giving a brown slurry. Repeated washing of the yellow-brown powder with pentane yielded 0.0173 g (20.%). X-ray quality crystals were grown from C_6D_6. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.94 (s), 6.90 (s), 4.05 (m), 2.29 (s), 2.25 (s), 1.88 (m), 1.61 (m), 1.13 (m). ^{13}C NMR (125 MHz, $CDCl_3$, 35, 800 scans, δ): 479.64, 292.79, 212.98, 212.31, 138.62, 138.52, 138.29, 138.20, 135.41, 129.59, 129.50, 52.64, 52.23, 52.20, 51.14, 48.08, 31.41, 31.26, 29.92, 29.53, 28.17, 28.09, 26.58, 25.85, 21.50, 21.20, 19.98, 18.96. ^{31}P NMR (500 MHz, $CDCl_3$, δ): 32.0 (s). FAB-MS (NBA matrix): *m/z* [isotope cluster consistent with the primary species $M + H^+$] calcd for $C_{40}H_{60}N_2Cl_2PRu$, 771.88; found [$M + H^+$] 771.4.

(17) Structural data: Monoclinic *P*21/*n*, $a = 11.7787(4)$ Å, $b = 21.2005(8)$ Å, $c = 17.3676(7)$ Å, $\beta = 94.669(2)°$, $V = 4322.5(3)$ Å^3, 100(2) K, 13 007 independent reflections (Mo Kα), R1 = 0.0327, wR2 = 0.0882.

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