

A Bimetallic Ru₂Pt Complex Containing a Trigonal-Planar μ_3 -Carbido Ligand: Formation, Structure, and Reactivity Relevant to the Fischer–Tropsch Process

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In contrast to the common occurrence of trigonal sp²-hybridized carbon atoms in covalent substances, transition-metal complexes that contain a planar three-coordinate carbon as a ligand are extremely rare.^{1,2} This essentially unexplored class of complexes should provide an interesting analogy to metal carbene³ and carbyne⁴ complexes [i.e., L_nM=CR₂ and L_nM(μ_2 -CR)ML_n, respectively] and serve as useful models of transition-metal surface carbide species, as exemplified by other complexes of low-coordinate carbides.^{1,2,5–10} Herein we report the synthesis and structure of a bimetallic Ru₂Pt complex that contains a trigonal-planar μ_3 -carbido ligand generated by a double C–H bond activation of a cluster-bound μ_2 -methylene ligand.^{9,10} The resulting μ_3 -carbido ligand exhibited a reactivity relevant to the Fischer–Tropsch process,^{11–14} producing a μ_2 -ethylidene ligand via coupling with nearby methyl and hydride moieties.

Treatment of the cluster [(Cp*₂Ru)₂(μ_2 -CH₂)(μ_3 -NPh)Pt(PMe₃)₂] (**1**; Cp* = η^5 -C₅Me₅)¹⁵ with MeOTf in Et₂O afforded the cationic methyl derivative **2** in 85% yield (Scheme 1). Single-crystal X-ray diffraction (XRD) analysis of **2** revealed the terminal coordination of the methyl ligand to a Ru center. Although complex **2** showed no signs of reaction when heated in toluene at 110 °C for 24 h, complex **2** underwent a facile thermal isomerization reaction to produce the carbido complex [(Cp*₂Ru)₂(μ_2 -NHPh)(μ_2 -H)(μ_3 -C)PtMe(PMe₃)₂][OTf] (**3**) when heated for 3 days at 40 °C in a toluene suspension (Scheme 1). Repeating the reaction using ¹³C-enriched **2**, [(Cp*₂Ru)₂CH₃(μ_2 -¹³CH₂)(μ_3 -NPh)Pt(PMe₃)₂][OTf] (**2**-¹³CH₂), resulted in exclusive enrichment at the μ_3 -carbido carbon in **3**, demonstrating that the μ_3 -carbido ligand in **3** arises from the μ_2 -CH₂ ligand in **2**. Complex **3** was isolated in 93% yield as a red

and 8 Hz, ¹J_{PtC} = 858 Hz). This ¹³C chemical shift is similar to those reported for the μ_3 -C ligand in [KCMo(NR_{Ar})₃]₂ [δ 482.8; R = CMe(CD₃)₂, Ar = 3,5-C₆H₃Me₂]¹ and the μ_2 -CH ligand in [Cp₂Fe₂(CO)₃(μ_2 -CH)][PF₆] (δ 490.2).^{4a} A signal due to the Pt–Me carbon was observed at δ 3.7 (²J_{PC} = 76 and 8 Hz, ¹J_{PtC} = 557 Hz). In the ¹H NMR spectrum of **3**, resonances attributable to the Ru-bound hydride and the amido N–H proton were observed at δ –18.7 (s) and 6.17 (br s), respectively.

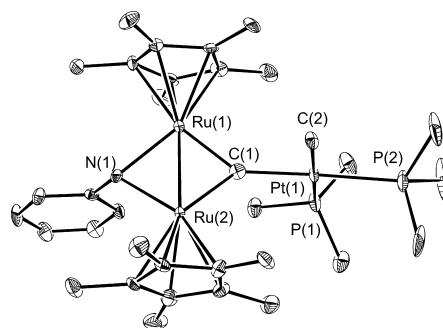


Figure 1. ORTEP drawing of the cationic part of **3** (50% probability level). H atoms have been omitted. Selected bond lengths (Å) and angles (deg): Ru(1)–C(1), 1.943(7); Ru(2)–C(1), 1.959(7); Pt(1)–C(1), 1.993(7); Pt(1)–C(2), 2.111(6); Ru(1)–N(1), 2.086(5); Ru(2)–N(1), 2.081(5); Pt(1)–P(1), 2.3094(17); Pt(1)–P(2), 2.3171(18); Ru(1)–C(1)–Ru(2), 77.6(3); Ru(1)–C(1)–Pt(1), 143.6(4); Ru(2)–C(1)–Pt(1), 137.9(4).

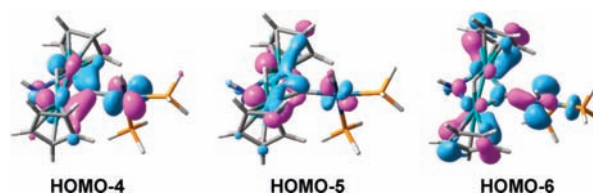
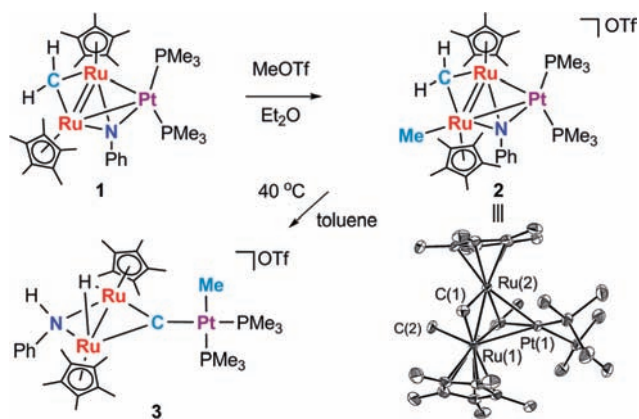


Figure 2. Highest occupied MOs involved in σ and π bonding of the μ_3 -carbido ligand in [(CpRu)₂(μ_2 -H)(μ_2 -NH₂)(μ_3 -C)PtH(PMe₃)₂]⁺.

Scheme 1

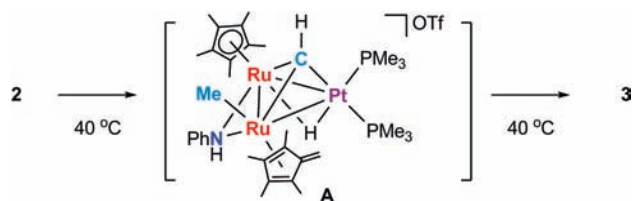


crystalline solid and characterized by elemental analysis, multinuclear NMR spectroscopy (¹H, ¹³C{¹H}, and ³¹P{¹H}), and single-crystal XRD. The ¹³C{¹H} NMR spectrum of **3** showed a downfield resonance assignable to the carbido carbon at δ 464.6 (²J_{PC} = 110

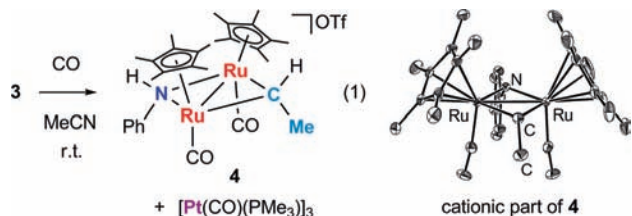
A thermal ellipsoid plot of the cationic part of **3** is shown in Figure 1. The carbon atom C(1) has trigonal-planar geometry (sum of the bond angles = 359.1°) and acts as a link between the Ru₂ and Pt fragments to form a Y-shaped Ru₂(μ_3 -C)Pt core. The Ru–C(1) distances in **3** [1.943(7) and 1.959(7) Å] are shorter than the Ru–C single-bond lengths observed for the μ_2 -methylene ligand in **2** [2.034(4) and 2.043(5) Å] and are analogous to the Ru–C distances observed for the μ_2 -ethylidene ligand in [Cp*₂Ru(μ_2 -CMe)(μ_2 -NPh)RuCp*][OTf] [1.929(7) and 1.914(7) Å].¹⁶ The Pt–C(1) distance in **3** [1.993(7) Å] is similar to that reported for [(IMes)Pt(dmsO)Cl₂] [1.981(8) Å; IMes = 1,3-dimesitylimidazolidine-2-ylidene],¹⁷ in which the N-heterocyclic carbene acts as a σ -donor ligand. Other structural features include the pyramidal geometry of N(1), indicating its formulation as a μ_2 -amido nitrogen,

and the folding of the Ru(1)–N(1)–Ru(2)–C(1) ring, which suggests the existence of a μ_2 -hydride ligand between the Ru atoms [dihedral angle between the Ru–N(1)–C(1) planes = 153.3°].

A density functional theory (DFT) calculation was conducted on a simplified model of **3**, [(CpRu) μ_2 (H) μ_2 (NH₂)(μ_3 -C)PtH(PMe₃)₂]⁺. The four highest occupied molecular orbitals (HOMOs) are predominantly metal-centered and contribute little to metal–ligand bonding. The next HOMOs (Figure 2) represent bonding between the carbido ligand and the metal centers. HOMO-4 and HOMO-5 represent Ru–C σ and π bonds, respectively, in the Ru(μ_3 -C)Ru moiety, showing the multiple-bond nature of the Ru–carbido bonds. Both of these orbitals have repulsive π interactions with respect to the Pt–carbido bond. Thus, the Pt–carbido bond is made chiefly by σ interactions, as represented by HOMO-6. Recently, an analogy between the ruthenium terminal carbido complex [(C₃P)₂Cl₂RuC] and carbon monoxide has been proposed,^{8g} and an adduct of this complex with a {PdCl₂(SMe₂)} fragment has been isolated.^{8b} The diruthenium carbido fragment {(Cp*Ru) μ_2 (H) μ_2 (NHPH)(μ_3 -C)} in **3** seems to be analogous to π -donor-stabilized carbenes,¹⁸ since the carbido carbon atom is sp²-hybridized, has π bonds with the adjacent Ru centers, and serves as a two-electron σ -donor to the 14-electron {PtMe(PMe₃)₂}⁺ fragment.



A possible intermediate was detected by NMR spectroscopy during the course of the conversion of **2** into **3**.¹⁹ This species has not been isolated but has been formulated as the μ_3 -methyne- μ_2 -hydride fulvene complex **A** on the basis of ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy. Signature data include the μ_3 -CH resonances [δ (¹³C) = 279.1, ²J_{PC} = 63 Hz,²⁰ ¹J_{PtC} = 502 Hz; δ (¹H) = 14.6, ³J_{PH} = 11.6 and 2.0 Hz, ²J_{PH} = 56.4 Hz, ¹J_{CH} = 160.8 Hz] and the μ_2 -hydride resonance [δ (¹H) = –15.5, ²J_{PH} = 66.8 and 15.6 Hz, ¹J_{PH} = 442 Hz]. ¹H NMR signals attributable to the tetramethylfulvene ligand were observed at δ 0.64, 1.25, 1.27, and 2.33 (s, 3H each) and δ 1.78 (m, 2H). Studies aimed at isolating **A** and understanding its reactivity are currently in progress.



C–C and C–H bond-forming reactions of metal carbido species have been the focus of numerous experimental^{16a–c,7c,d,8d–f,11,12} and theoretical^{13,14} studies. The carbido complex **3** reacted with 1 atm CO at room temperature to produce the dinuclear ethylidene complex **4**, which was isolated in 60% yield as yellow needles and characterized by single-crystal XRD.²¹ The major Pt-containing product was identified as the known triplatinum complex [Pt(CO)(PMe₃)₃] by IR, ¹H NMR, and ³¹P{¹H} NMR spectroscopy.²² The mechanism of this reaction is uncertain, but the reaction can

be viewed as involving C–H and C–C bond-forming reductive eliminations involving C, H, and Me ligands. The fact that the reaction is induced by coordination of CO may suggest a role for CO adsorption in facilitating the coupling of surface-bound C, H, and CH_x species in the Fischer–Tropsch hydrocarbon synthesis.^{11–14}

In summary, a planar three-coordinate carbido ligand has been generated on a bimetallic Ru₂Pt cluster via double C–H activation of a bridging methylene ligand. XRD and DFT studies indicated the existence of delocalized Ru–C π bonds and an N-heterocyclic carbene-like Pt–C bond in the μ_3 -CRu₂Pt moiety. A reactivity study revealed CO-promoted coupling of the carbido ligand with a hydride and methyl ligands to form an ethylidene moiety.

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Supporting Information Available: Experimental procedures, characterization data, computational details, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) The amount of **A** present in the reaction mixture was consistently small (<10%) during the course of the conversion of **2** to **3** in toluene, probably because of the low solubility of **2** and **3** in toluene. In contrast, when **2** was heated in CD₃CN solution at 40 °C, much larger amount of **A** (~50%) was generated along with unreacted **2** (~30%) and carbide **3** (~10%). Heating the mixture of these complexes in toluene at 40 °C for 2 days gave **3** in 80% NMR yield.
- (20) ²J_{PC} coupling with another phosphorus nucleus was not resolved.
- (21) The XRD study was done after anion exchange from OTf⁻ to BPh₄⁻.
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