Synthesis and structural characterization of a tetrahedral sp^3 carbide cluster compound

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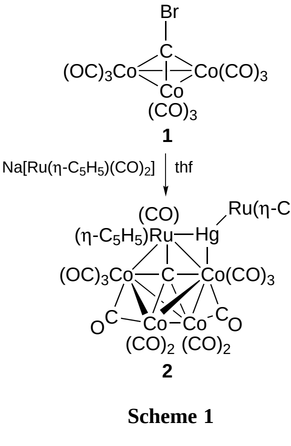
Treatment of the (μ_3-halomethylidyne)tricobalt cluster compound (μ_3-X–C)$Co_3(CO)_6L_3$ with Na[Ru(η-C_5H_5)$(CO)_2$] produces the heptanuclear (μ_5-C)(η-C_5H_5)$_2$$Ru_2Co_4Hg(CO)_{13}$ 2 [X = Br; L_3 = $(CO)_3$] and tetranuclear carbide cluster compound (η-C_5H_5)$(CO)_2$Ru(μ_4-C)$Co_3(CO)_6$(tdpm) 4 [X = Cl; L_3 = CH$(PPh_2)_3$ (tdpm)], *via* substitution of μ_3-X–C; the latter complex 4 is the first example of a structurally characterized tetrahedral sp^3 carbide cluster compound.

Transition-metal carbide cluster compounds have been studied extensively over twenty years as model compounds for a carbide species adsorbed on a metal surface.[1,2] Previous studies have revealed various aspects of such a species as a pivotal intermediate in catalytic transformations of hydrocarbons and carbon monoxide (*e.g.* conversion to CH_x species through H-addition).[3] However, the carbido carbon atoms in the previous examples are partly or completely encapsulated in a metal array such as butterfly and octahedral structures.[1] To the best of our knowledge, no example of a structurally characterized carbide cluster compound with an sp^3-hybridized carbido carbon atom has been reported so far,[4,5] although it would be the most probable structure that an organic chemist expects. Our research interest has been focused on synthetic study toward polymetallic compounds with a simple carbon linkage such as permetallated ethane, ethene and ethyne,[6] and herein we report the synthesis of the first structurally characterized example of a tetrahedral sp^3 carbide cluster compound, a permetallated methane.

The synthetic method that we have employed is nucleophilic substitution of the classical (μ_3-halomethylidyne)tricobalt cluster derivatives, (μ_3-X–C)$Co_3(CO)_6L_3$,[7] by a metal anion.[5a,8] When the (μ_3-bromomethylidyne)nonacarbonyl derivative, (μ_3-Br–C)$Co_3(CO)_9$ **1** [X = Br; L_3 = $(CO)_3$] was treated with the ruthenate, Na[Ru(η-C_5H_5)$(CO)_2$], in thf, a heptanuclear carbide cluster compound (μ_5-C)(η-C_5H_5)$_2$$Ru_2Co_4Hg(CO)_{13}$ **2** was obtained in low yield (*ca.* 10%) by way of replacement of Br and addition of metal fragments (Scheme 1).† The molecular structure determined by X-ray crystallography (Fig. 1) contains a carbido carbon atom which is encapsulated in the pentanuclear RuCo$_4$ wingtip-bridged butterfly structure.‡ Interaction of one of the two Ru–Co edges with the [HgRu(η-C_5H_5)$(CO)_2$]$^+$ fragment, which is isolobal with H$^+$, causes slight elongation of the Ru(1)–Co(1) bond [2.937(2) Å; *cf.* Ru(1)–Co(4) 2.837(3) Å] owing to a three-center–two-electron interaction. Judging from the Co(1)–C(1)–Co(4) [165.0(10)°] and M_{ax}–C(1)–M_{eq} angles [82–99°: M_{ax} = Co(1), Co(4)], the coordination structure of the central carbido carbon atom can be described as distorted trigonal bipyramidal with a Ru(1)–Co(2)–Co(3) equatorial plane. This type of (μ_5-C)M_5 structure has several precedents.[8] The mechanism of formation of **2** should involve initial nucleophilic substitution of **1** with the ruthenate giving a tetrahedral carbide intermediate, which picks up Co$(CO)_n$ and [HgRu(η-C_5H_5)$(CO)_2$]$^+$ fragments present in a reaction mixture§ to form the electron-precise species **2** with 76 cluster valence electrons (the wingtip-bridged butterfly RuCo$_4$ core). The formation of **2** suggests susceptibility of the μ_3-CBr moiety in **1** toward nucleophilic substitution, and similar reactions affording encapsulated carbide cluster compounds have already been reported.[9]



Scheme 1

In order to prevent the tricobalt unit from fragmentation and cluster core expansion, the three cobalt atoms were linked together by a tripodal ligand, tris(diphenylphosphino)methane (tdpm). Treatment of the μ_3-chloromethylidyne cluster supported by tdpm, (μ_3-Cl–C)$Co_3(CO)_6$(tdpm) **3** [X = Cl; L_3 = tdpm],¶ with Na[Ru(η-C_5H_5)$(CO)_2$] in thf gave the brown complex **4** (5–10%) along with the μ_3-methylidyne complex, (μ_3-H–C)$Co_3(CO)_6$(tdpm) **5**, after chromatographic separation (Scheme 2).† A ^{1}H NMR spectrum of **4** containing a η-C_5H_5 signal (δ 5.81) in addition to signals from tdpm [δ 5.77 (1 H, q, J_{PH} 6.1 Hz, P$_3$CH), 6.7–7.3 (30 H, m, Ph$_6$)] is consistent with

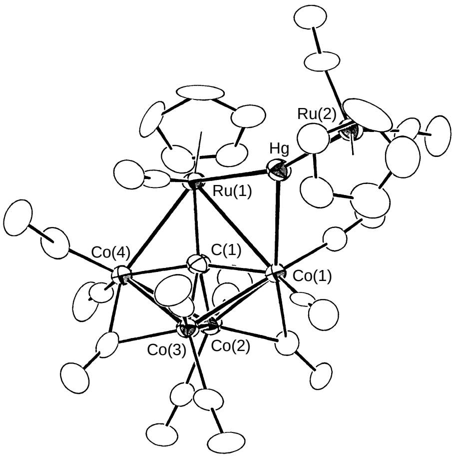
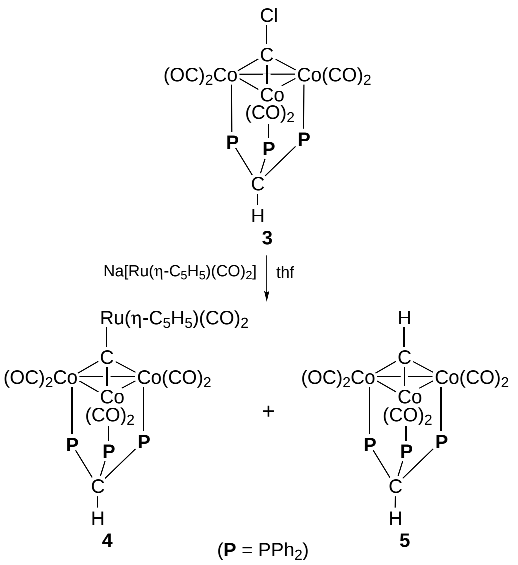


Fig. 1 Molecular structure of **2** drawn at the 30% probability level. Important bond lengths (Å) and angles (°): C(1)–Ru(1) 1.97(2), C(1)–Co(1) 1.86(2), C(1)–Co(2) 1.95(2), C(1)–Co(3) 1.93(2), C(1)–Co(4) 1.87(2), Ru(1)–C(1)–Co(1) 99.6(7), Ru(1)–C(1)–Co(2) 139.1(9), Ru(1)–C(1)–Co(3) 142.2(9), Ru(1)–C(1)–Co(4) 95.4(7), Co(1)–C(1)–Co(2) 82.7(6), Co(1)–C(1)–Co(3) 86.6(6), Co(1)–C(1)–Co(4) 165.0(10), Co(2)–C(1)–Co(3) 78.6(6), Co(2)–C(1)–Co(4) 85.4(6), Co(3)–C(1)–Co(4) 82.1(6).



Scheme 2

the expected structure, $(\eta\text{-}C_5H_5)(CO)_2Ru(\mu_4\text{-}C)Co_3(CO)_6(tdpm)$, which is supported by the single ^{31}P NMR resonance (δ 39.0) and established by X-ray crystallography (Fig. 2).‡ The central carbido carbon atom [C(1)] is bonded to the distal Ru atom and the basal Co_3 triangle through σ bonds [C(1)–Ru 2.122(8) Å, C(1)–Co 1.887–1.924(9) Å]. Although the Ru–C(1)–Co [129.2–132.9(5)°] and Co–C(1)–Co angles [80.4–81.6(3)°] deviate from the ideal tetrahedral angle (109.4°) owing to the fact that the Co atoms are linked together by metal–metal bonds, the hybridization of the central carbido carbon atom is found to be close to sp^3. Thus the tetranuclear complex **4** has been characterized as a tetrahedral sp^3 carbide cluster compound, a permetallated methane. The formation of the μ_3-CH compound **5** suggests participation of a radical mechanism initiated by electron transfer from the ruthenate to **3**. Coupling of the resulting radical species, $^{\cdot}(\mu_3\text{-}C)Co_3(CO)_6(tdpm)$ and $^{\cdot}Ru(\eta\text{-}C_5H_5)(CO)_2$, would furnish **4**, but H-abstraction from the reaction medium may give rise to **5**.

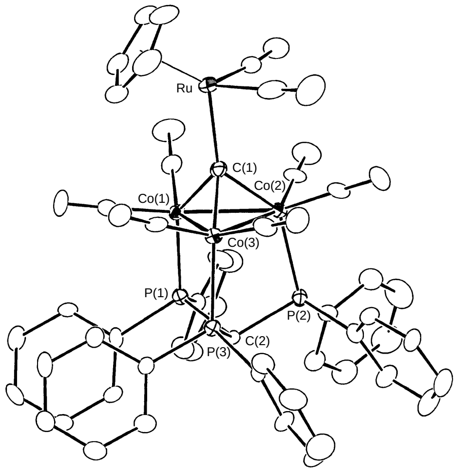


Fig. 2 Molecular structure of **4** drawn at the 30% probability level. Important bond lengths (Å) and angles (°): C(1)–Ru 2.122(8), C(1)–Co(1) 1.887(9), C(1)–Co(2) 1.924(8), C(1)–Co(3) 1.912(9), Ru–C(1)–Co(1) 129.2(4), Ru–C(1)–Co(2) 132.9(5), Ru–C(1)–Co(3) 132.2(5), Co(1)–C(1)–Co(2) 80.9(3), Co(2)–C(1)–Co(3) 80.4(3), Co(3)–C(1)–Co(1) 81.6(3).

In conclusion, the present study has revealed the versatility of the synthetic method for carbide cluster compounds *via* nucleophilic displacement of halogenomethylidyne clusters with metalates, and the first example of a structurally characterized tetrahedral sp^3 carbide cluster has been prepared successfully by this method.

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Footnotes and References

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† *Spectral data*: for **2**: $\delta_H(CDCl_3)$ 5.20, 5.22 (s, $C_5H_5 \times 2$); IR (CH_2Cl_2); ν(C≡O) 2073, 2037, 2021, 1974, 1948, 1848 cm^{-1}; FDMS: *m/z* 1145 (M^+). For **4**: IR (CH_2Cl_2), ν(C≡O) 2034, 1986, 1972, 1938 cm^{-1}; FDMS: *m/z* 1146 (M^+). Attempted measurement of $\delta_C(\mu\text{-}C)$ of **2** and **4** was unsuccessful owing to the ^{59}Co quadrapole moment and ^{31}P coupling.

‡ X-Ray diffraction measurements of **2** were made on a Rigaku RAXIS IV imaging plate area detector with graphite-monochromated Mo-Kα radiation. *Crystal data* for **2**: $C_{24}H_{10}Co_4HgO_{13}Ru_2$ M = 1144.8, T = 25 °C, monoclinic, space group $C2/c$, a = 39.95(1), b = 8.606(2), c = 18.22(2) Å, β = 101.44(7)°, U = 6139(5) $Å^3$, Z = 8, D_c = 2.48 g cm^{-3}, μ = 81.2 cm^{-1}, $R(R_w)$ = 0.110(0.161) for all the 5773 unique data and 392 parameters (on F^2). X-Ray diffraction measurements of **4** were made on a Rigaku AFC7R automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation. *Crystal data* for **4**·$2C_6H_5Me$: $C_{65}H_{52}Co_3O_8P_3Ru$, M = 1331.9, T = −70 °C, orthorhombic, space group $P2_12_12_1$, a = 19.565(3), b = 23.763(5), c = 12.544(3) Å, U = 5832(4) $Å^3$, Z = 8, D_c = 1.52 g cm^{-3}, μ = 12.3 cm^{-1} $R(R_w)$ = 0.085(0.087) for all the 5677 unique data and 635 parameters (on F^2). CCDC 182/524.

§ The $[HgRu(\eta\text{-}C_5H_5)(CO)_2]^+$ fragment may arise from $Hg[Ru(\eta\text{-}C_5H_5)(CO)_2]_2$, a byproduct of the synthesis of $Na[Ru(\eta\text{-}C_5H_5)(CO)_2]$ by Na-amalgam reduction. $Hg[Ru(\eta\text{-}C_5H_5)(CO)_2]_2$ was isolated from the reaction mixture and characterized by X-ray crystallography.

¶ Complex **3** was prepared by thermal reaction of $(\mu_3\text{-}Cl\text{-}C)Co_3(CO)_9$ with tdpm. Attempted synthesis of the bromo derivative by reaction of **1** with tdpm did not afford the expected product but the zwitterionic cyclic adduct, $Co_3(CO)_6(\mu\text{-}PPh_2)(\mu_3\text{-}CPPh_2CH_2PPh_2)$, the formation of which also involved nucleophilic displacement at the μ_3-Br–C moiety. M. Akita, Y. Takahashi and Y. Moro-oka, unpublished work.

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