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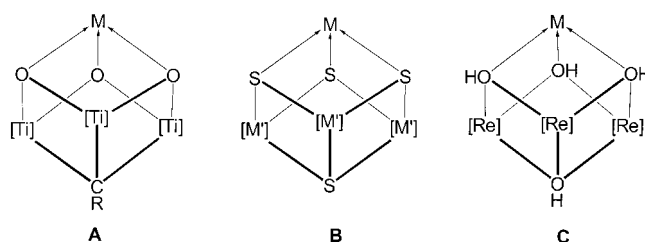
Construction of Heterometallic Cubanes

**$[\{\text{Ti}_3\text{Cp}^*(\mu_3\text{-CR})\}(\mu_3\text{-O})_3\{\text{Mo}(\text{CO})_3\}]$
 ($\text{R} = \text{H, Me}$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and
 $[\{\text{Ti}_3\text{Cp}^*(\mu_3\text{-N})\}(\mu_3\text{-NH})_3\{\text{M}(\text{CO})_3\}]$
 ($\text{M} = \text{Cr, Mo, W}$); Crystal Structure of
 $[\{\text{Ti}_3\text{Cp}^*(\mu_3\text{-CMe})\}(\mu_3\text{-O})_3\{\text{Mo}(\text{CO})_3\}]^{**}$**

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*Dedicated to Alexander von Humboldt
 on the occasion of his commemorative year 1999*

Until now we have focused on the rich chemistry of alkylidyne groups on a trinuclear support without metal–metal bonds $[\{\text{TiCp}^*(\mu\text{-O})\}_3(\mu_3\text{-CR})]$ ($\text{R} = \text{H}$ (**1**), Me (**2**); $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). We showed that metal carbonyl hydrides and unsaturated molecules such as carbon monoxide, isocyanides, and ketones are incorporated into the Ti_3O_3 core with direct participation of the alkylidyne units.^[1] In the course of our studies, we discovered that these complexes can also act as macrocyclic, tridentate six-electron donor ligands (Scheme 1, **A**) and thus provide an effective route to heterocubanes with $\text{MTi}_3(\mu_3\text{-CR})(\mu\text{-O})_3$ cores. To our knowledge, the only comparable behavior is the incorporation of metal ions by the

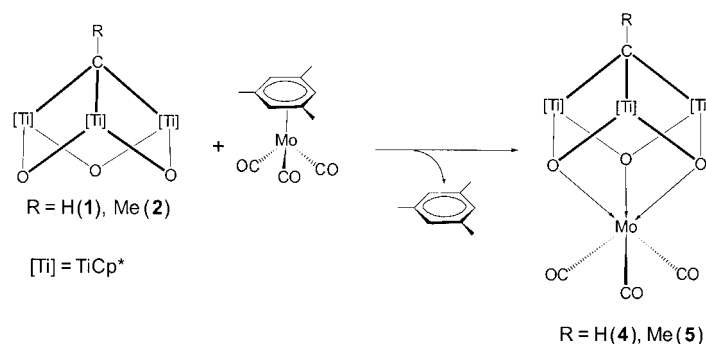


Scheme 1. Precubane systems as tripodal ligands.

$\text{M}'_3\text{S}_4$ ($\text{M}' = \text{Fe, Mo}$) precubane clusters (Scheme 1, **B**), which leads to heterometallic cubane-type $\text{MM}'_3\text{S}_4$ cores,^[2] and the hydroxymetalate complex $[\text{Re}_3(\text{CO})_9(\mu\text{-OH})_3(\mu_3\text{-OH})]$, which acts as a tripodal ligand (Scheme 1, **C**) to form “double-cubane” structures.^[3] Furthermore, the $(\mu_3\text{-CR})\text{Ti}_3(\mu_3\text{-O})_3\text{Mo}(\text{CO})_3$ cores described here could be invaluable as discrete and ideal models of oxide-supported metal carbonyl complexes for studying the catalyst–support interaction.^[4]

Here we report the formation of the heterometallic cubanes $[\{\text{Ti}_3\text{Cp}^*(\mu_3\text{-CR})\}(\mu_3\text{-O})_3\{\text{Mo}(\text{CO})_3\}]$ ($\text{R} = \text{H}$ (**4**), Me (**5**)) and $[\{\text{Ti}_3\text{Cp}^*(\mu_3\text{-N})\}(\mu_3\text{-NH})_3\{\text{Mo}(\text{CO})_3\}]$ (**6**) from $[\text{Mo}(\text{CO})_3(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]$ and the alkylidyne complexes **1** and **2** and the isoelectronic $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**3**), respectively. Treatment of **3** with the hexacarbonyl complexes $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr, Mo, W}$) also leads to **6** and the analogous heterocubane derivatives $[\{\text{Ti}_3\text{Cp}^*(\mu_3\text{-N})\}(\mu_3\text{-NH})_3\{\text{M}(\text{CO})_3\}]$ ($\text{M} = \text{W}$ (**7**), Cr (**8**)).

Reaction of the trimetallic starting materials **1** and **2** with one equivalent of $[\text{Mo}(\text{CO})_3(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]$ ^[5] in hexane at 80 °C for four days led to displacement of the mesitylene ligand from molybdenum to afford in good yield the dark green crystalline heterocubanes **4** and **5**, respectively (Scheme 2). The solid compounds are stable under argon at room temperature but decompose slowly (months) in $[\text{D}_6]\text{benzene}$ with formation of **1** or **2**.^[6]



Scheme 2. Synthesis of the heterometallic cubane complexes **4** and **5**.

The ^{13}C NMR spectra of both complexes show one signal at $\delta \approx 227$ for the three equivalent terminal carbonyl groups and exhibit a downfield shift of the alkylidyne carbon signals ($\delta(\mu_3\text{-CR}) = 410.3$ (**4**), 434.8 (**5**) relative to **1** ($\delta(\mu_3\text{-CH}) = 383.2$) and **2** ($\delta(\mu_3\text{-CMe}) = 401.7$). In the IR spectra of these compounds, the three terminal CO groups give rise to two strong bands between 1915 and 1815 cm^{-1} , as expected for complexes containing a *fac*- $\text{Mo}(\text{CO})_3$ group.^[7]

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The molecular structure of **5** was determined by X-ray diffraction (Figure 1)^[8, 9] and revealed a heterometallic cubane in which the molybdenum tricarbonyl moiety is linked to the ethylidyne complex **2** through the three bridging oxygen atoms. The bond lengths and angles of **5** are quite similar to

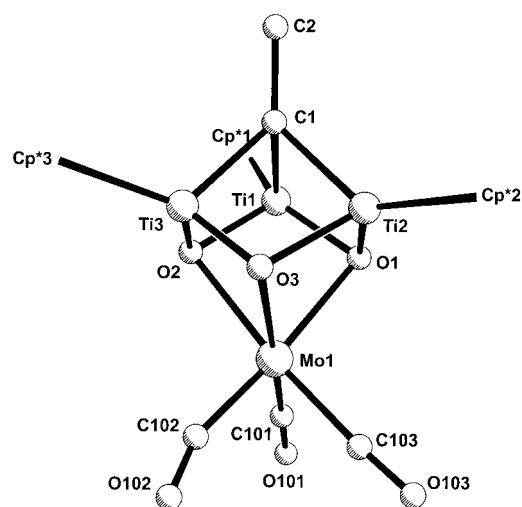
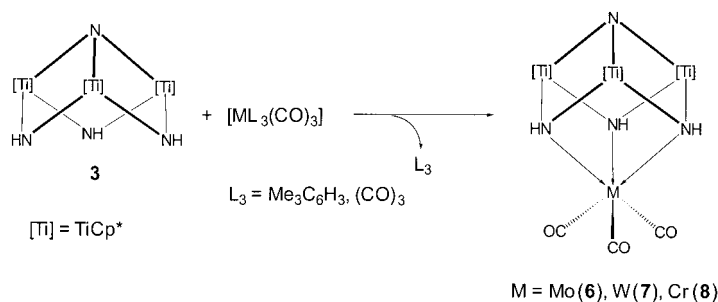


Figure 1. Simplified view of the molecular structure of complex **5**. Selected average bond lengths [Å] and angles [°]: Mo–O 2.308(15), Mo–C 1.92(4), Mo...Ti 2.998(4), Ti–Cp* 2.090, Ti...Ti 2.856(5); Cp*–Ti–C1 125.3, C1–Ti–O 86.8(8), Ti–O–Ti 100.4(7), O–Ti–O 99.0(7), Ti–O–Mo 91.4(7), O–Mo–O 75.4(5). Cp* = η^5 -C₅Me₅. Cp* groups are omitted for clarity.

those of the parent compound **2** (see Supporting Information),^[10] with the exception of the O–Ti–O angles, which are approximately 4° smaller in **5**. This similarity is also exhibited by the complexes [Fe₃S₄S₃]^[11] (S^γ refers to the sequence position of the cysteine residue) and [NEt₄]₃[[Fe₃(SET)₃](μ₃-S)₃Mo(CO)₃]₃;^[12] a precubane behavior of the former was invoked.^[2g] Thus, the alkylidyne complex **2** acts like a preorganized ligand^[13] that donates electron density to the molybdenum atom through the three electron-rich bridging oxygen atoms to give a heterometallic (μ₃-CR)Ti₃(μ-O)₃Mo cubane core.

As might be anticipated from its isoelectronic and isostructural relationship to **1** and **2**, the trinuclear nitrido complex **3**^[14] reacts slowly at room temperature with [Mo(CO)₃(1,3,5-Me₃C₆H₃)] or by irradiation with [M(CO)₆] (M = Cr, Mo, W) to give the crystalline heterocubanes **6–8**, analogous to the oxoalkylidynes **4** and **5** (Scheme 3). Complexes **6–8** are thermally stable under argon both in the solid state and in



Scheme 3. Synthesis of the heterometallic cubane complexes **6–8**.

solution. Heating them in solution in [D₆]benzene to 100 °C causes no decomposition.

The IR spectra of **6–8** show a N–H band at about 3360 cm^{−1}, and the carbonyl region is practically identical to those of **4** and **5**. Their ¹³C NMR spectra contain signals attributable to the three equivalent Cp* ligands and the M(CO)₃ fragments. The ¹H NMR spectra of **6–8** and the ¹⁵N NMR spectrum of [[Ti₃Cp₃(μ₃-¹⁵N)](μ₃-¹⁵NH)₃[Mo(CO)₃]] (¹⁵N)**6**) displayed signals at δ(μ₃-NH) = 11.5 (**6**), 11.4 (**7**), 10.9 (**8**), δ(μ₃-¹⁵NH) = −13.7, and δ(μ₃-¹⁵N) = 399.2.

To understand the electronic structures of these heterocubane compounds, their optimal geometries were calculated by density functional theory (DFT) methods on the model compounds [[Ti₃Cp₃(μ₃-CH)](μ₃-O)₃[Mo(CO)₃]] (**4'**; Cp = η^5 -C₅H₅) and [[Ti₃Cp₃(μ₃-N)](μ₃-NH)₃[Mo(CO)₃]] (**6'**). The analogous chromium and tungsten clusters were also investigated.^[15–19] The experimental geometry of complex **4** is well reproduced by the DFT calculations. The largest deviation between experimental and theoretical bond lengths is in the Ti...Mo distances; the calculated value is 0.082 Å shorter than the experimental value. The analysis of the orbitals of **4'** indicates that this cluster has six electrons from the metal (Figure 2), four of which are in orbitals of e symmetry and two

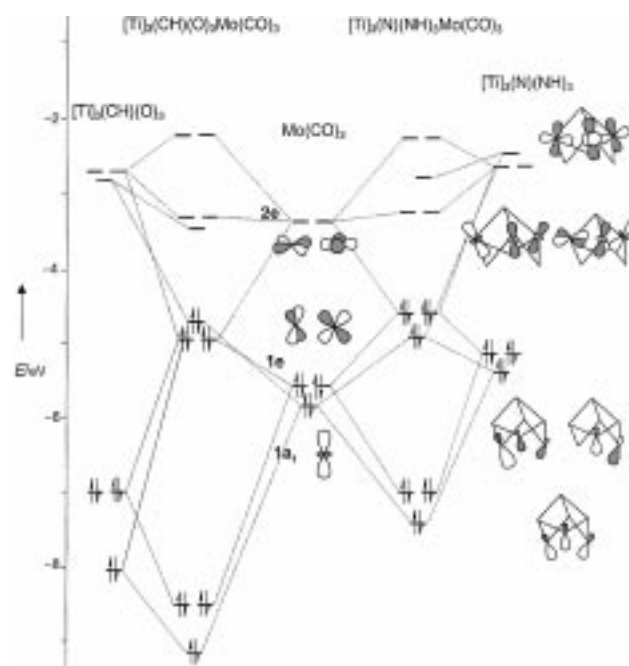


Figure 2. Interaction orbital diagram for the complexes **4'** and **6'**. [Ti] represents TiCp.

in an orbital of a₁ symmetry. The contributions of molybdenum to these orbitals are about 84 and 88% (Mulliken), respectively. The LUMO has a₁ symmetry and is a bonding combination of titanium d orbitals. These results clearly confirm that the formation of the cluster is not accompanied by oxidation of the molybdenum center and, as in the precubane precursor, the oxidation state of the titanium atom is still +4. Although the oxidation state of molybdenum should be regarded as zero, the Mo atom shares electron

density by means of metal–metal coupling with the Ti_3 unit, mainly through molybdenum orbitals of e symmetry. The elongation of the $\text{Mo}\cdots\text{Ti}$ distances by 0.1 Å when one electron is removed from the doubly degenerate metal orbitals reveals the presence of a positive metal–metal interaction. Harris et al.^[20] reported similar charge delocalization in the cubane-type clusters $[\text{MMo}_3\text{S}_4]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Co}$).

The energy of dissociation of **4'** to give the fragments $[\{\text{Ti}_3\text{Cp}_3(\mu_3\text{-CH})\}(\mu\text{-O})_3]$ and $[\text{Mo}(\text{CO})_3]$ was calculated to be +216.7 kJ mol^{−1}. The equivalent process for **6'** requires 134 kJ mol^{−1} more. We can rationalize this major energy difference by means of the orbital interaction diagram given in Figure 2. The higher energy of the NH lone pairs (−5.10 and −5.39 eV) relative to oxygen (−6.96 and −8.08 eV) favors σ donation from the ligand to the molybdenum fragment and therefore stabilization of the ligand lone pairs. In turn, the energy of the 1e orbitals of the molybdenum fragment increases, and this favors its interaction with the unoccupied titanium orbitals of the trinuclear ligand.

When chromium or tungsten replaced molybdenum in **4'**, the behavior was similar, but the dissociation energies were somewhat higher. The calculated values were 249.4 kJ mol^{−1} for the chromium and 287.5 kJ mol^{−1} for the tungsten complex. The same trend was observed when this substitution was made in complex **6'**, for which the bonding energies were 375.7 and 444.8 kJ mol^{−1}, respectively. There is a relationship between the bonding energy and the sharing of the electrons on the metal by Mo– Ti_3 coupling. The greatest delocalization occurs in $[\{\text{Ti}_3\text{Cp}_3(\mu_3\text{-N})\}(\mu_3\text{-NH})_3\{\text{W}(\text{CO})_3\}]$, in which 0.86 e are transferred from the tungsten center to the Ti_3 core, 0.72 e through the degenerate orbitals on the metal and 0.14 e through the orbital of a_1 symmetry on the metal. The smallest charge transfer occurs in complex **4'**, in which about 0.5 e are transferred from the molybdenum center to the titanium atoms. The electron delocalization in the Ti_3M clusters could be associated with the relatively high wavenumbers of the three terminal CO ligands in these complexes.

The energies of the reactions in Schemes 2 and 3 ($\text{M} = \text{Mo}$, $\text{L}_3 = \text{C}_6\text{H}_6$) were also calculated. Whereas for the precubane $[\{\text{Ti}_3\text{Cp}_3(\mu_3\text{-CH})\}(\mu\text{-O})_3]$ the process is exothermic with a relatively small reaction energy of −29.7 kJ mol^{−1}, for the trinuclear nitride $[\{\text{Ti}_3\text{Cp}_3(\mu_3\text{-N})\}(\mu\text{-NH})_3]$ the process is largely exothermic with a reaction energy of −164.4 kJ mol^{−1}. This discrepancy could be the origin of the different stabilities of complexes **4–6**.

To our knowledge, these results represent the first examples of an unprecedented family of cubane clusters containing Ti_3M heterometallic cores. These compounds can be easily synthesized by reaction of the organometallic complexes **1–3** with appropriate metal carbonyl complexes. Calculations showed that although the formation of complexes **4–8** is not accompanied by changes in the oxidation state of the metal centers, the metal carbonyl fragment shares electron density with the titanium atoms by means of metal–metal interactions. We believe that the trinuclear titanium complexes **1–3** offer many possibilities as *fac*-coordinating ligands, and we are now investigating the incorporation of diverse metal complex fragments.

Experimental Section

4: $[\text{Mo}(\text{CO})_3(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]$ (0.19 g, 0.64 mmol) was added to a solution of **1** (0.40 g, 0.65 mmol) in hexane (50 mL). The reaction mixture was heated at 80 °C for four days to give **4** as black crystals. Yield: 0.25 g (48 %). ¹H NMR (300 MHz, $[\text{D}_2]$ dichloromethane, 20 °C, TMS): $\delta = 2.01$ (s, 45H; C_5Me_3), 13.78 (s, 1H; CH); ¹³C NMR (75 MHz, $[\text{D}_2]$ dichloromethane, 20 °C): $\delta = 12.3$ (q, $J(\text{C},\text{H}) = 126.2$ Hz; C_5Me_3), 124.2 (m; C_5Me_3), 227.5 (s; CO), 410.3 (d, $J(\text{C},\text{H}) = 136.0$ Hz; $\equiv\text{CH}$); IR (KBr): $\tilde{\nu} = 2915$ (s), 1913 (vs) (CO), 1816 (vs) (CO), 1377 (s), 653 (s), 612 (s), 574 cm^{−1} (s); MS (EI, 70 eV): m/z (%): 791 (1) [M^+], 706 (3) [$\text{M}^+ - 3\text{CO}$], 610 (28) [$\text{M}^+ - \text{Mo}(\text{CO})_3$].

Compound **5** was prepared analogously to **4** from **2** (0.70 g, 1.12 mmol) and $[\text{Mo}(\text{CO})_3(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]$ (0.33 g, 1.11 mmol). Yield: 0.42 g (66 %). ¹H NMR (300 MHz, $[\text{D}_2]$ dichloromethane, 20 °C, TMS): $\delta = 2.00$ (s, 45H; C_5Me_3), 2.08 (s, 1H; CH); ¹³C NMR (75 MHz, $[\text{D}_2]$ dichloromethane, 20 °C): $\delta = 11.9$ (q, $J(\text{C},\text{H}) = 125.5$ Hz; C_5Me_3), 42.5 (q, $J(\text{C},\text{H}) = 125.5$ Hz; $\equiv\text{CMe}$), 124.2 (m; C_5Me_3), 226.8 (s; CO), 434.8 (s; $\equiv\text{CMe}$); IR (KBr): $\tilde{\nu} = 2915$ (s), 1911 (vs) (CO), 1818 (vs) (CO), 1376 (s), 632 (s), 614 (s), 583 cm^{−1} (vs); MS (EI, 70 eV): m/z (%): 704 (10) [$\text{M}^+ - 3\text{CO} - \text{CH}_4$], 624 (20) [$\text{M}^+ - \text{Mo}(\text{CO})_3$]; elemental analysis (%) calcd for $\text{C}_{35}\text{H}_{48}\text{MoO}_6\text{Ti}_3$ (804.40): C 52.26, H 6.02; found: C 52.71, H 6.14.

6: Method A: $[\text{Mo}(\text{CO})_3(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)]$ (0.30 g, 0.99 mmol) and **3** (0.60 g, 0.99 mmol) were dissolved in toluene (30 mL). The reaction mixture was stirred at room temperature for three days. Black crystals of **6** were obtained (0.55 g, 70 %). [¹⁵N]**6** was prepared by a similar method from $[\{\text{TiCp}^*(\mu\text{-}^{15}\text{NH})\}_3(\mu_3\text{-}^{15}\text{N})]$ ([¹⁵N]**3**). Method B: Compound **6** was prepared on an NMR-tube scale from **3** and $[\text{Mo}(\text{CO})_6]$ by using the same procedure as for **7**. ¹H NMR (300 MHz, C_6D_6 , 20 °C, TMS): $\delta = 1.86$ (s, 45H; C_5Me_3), 11.50 (br.s, 3H; NH); ¹³C{¹H} NMR (75 MHz, C_6D_6 , 20 °C): $\delta = 11.8$ (C_5Me_3), 118.9 (C_5Me_3), 230.7 (CO); ¹⁵N NMR (50.7 MHz, $\text{C}_6\text{D}_6/\text{CDCl}_3$, 20 °C):^[21] $\delta = -13.7$ (d, $J(\text{N},\text{H}) = 70.2$ Hz; $\mu_3\text{-NH}$), 399.2 (s; $\mu_3\text{-N}$); IR (KBr): $\tilde{\nu} = 3361$ (m) (NH), 2914 (s), 1915 (vs) (CO), 1822 (s) (CO), 1378 (s), 723 (s), 618 cm^{−1} (vs); MS (EI, 70 eV): m/z (%): 704 (41) [$\text{M}^+ - 3\text{CO}$]; elemental analysis (%) calcd for $\text{C}_{33}\text{H}_{48}\text{MoN}_4\text{O}_3\text{Ti}_3$ (788.4072): C 50.27, H 6.14, N 7.11; found: C 50.69, H 6.11, N 7.28.

7: Compound **3** (0.30 g, 0.49 mmol) and $[\text{W}(\text{CO})_6]$ (0.17 g, 0.49 mmol) were dissolved in toluene (60 mL) and irradiated with UV light for 4 h. The solution was concentrated and cooled to about −40 °C, and **7** was obtained as a reddish crystalline solid (0.18 g, 42 %). ¹H NMR (300 MHz, C_6D_6 , 20 °C, TMS): $\delta = 1.84$ (s, 45H; C_5Me_3), 11.39 (br.s, 3H; NH); ¹³C{¹H} NMR (75 MHz, C_6D_6 , 20 °C): $\delta = 11.8$ (C_5Me_3), 119.2 (C_5Me_3), 225.6 (CO); IR (KBr): $\tilde{\nu} = 3360$ (m) (NH), 2914 (s), 1914 (s) (CO), 1832 (s) (CO), 1378 (s), 724 (s), 616 cm^{−1} (s).

Compound **8** was prepared similarly to **7** from **3** (0.3 g, 0.49 mmol) and $[\text{Cr}(\text{CO})_6]$ (0.11 g, 0.49 mmol) with UV irradiation for 5 h. Yield: Black, crystalline **8** (0.21 g, 57 %). ¹H NMR (300 MHz, C_6D_6 , 20 °C, TMS): $\delta = 1.87$ (s, 45H; C_5Me_3), 10.90 (br.s, 3H; NH); ¹³C{¹H} NMR (75 MHz, C_6D_6 , 20 °C): $\delta = 11.8$ (C_5Me_3), 118.3 (C_5Me_3), 243.9 (CO); IR (KBr): $\tilde{\nu} = 3363$ (m) (NH), 2912 (s), 1911 (vs) (CO), 1829 (vs) (CO), 1377 (s), 719 (s), 630 (s), 620 cm^{−1} (s).

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- [8] X-ray structure determination of **5**: Dark green crystals of **5** were obtained by slow crystallization from a saturated solution in hexane. The data were collected on an Enraf Nonius CAD4 diffractometer at room temperature. Intensity measurements were performed by $\omega/2\theta$ scans in the range $3^\circ < \theta < 27^\circ$ on a crystal of dimensions $0.35 \times 0.28 \times 0.23$ mm. Of the 4409 measured reflections, 4193 were independent; largest minimum and maximum in the final difference Fourier synthesis: -1.063 and $1.621 \text{ e } \text{\AA}^{-3}$, $R1 = 0.107$ and $wR2 = 0.296$ (for 2496 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined as $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$. The structure was solved by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).^[9] Space groups $P2_1$ and $P2_1/m$ were used to solve and refine the structure, but only the former gave a sensible chemical structure due to disorder in the pentamethylcyclopentadienyl rings and the poor quality of the crystal (unfortunately, data could not be obtained at low temperature). However, this disorder did not affect the location of the core of the molecule. The hydrogen atoms were positioned geometrically and refined by using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134178. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Coupling of Alkynes on a Pd–Pd Bond to Generate an Electrophilic μ -Butenediylidene Moiety**

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In spite of its potential relevance to new palladium-catalyzed reactions, dipalladium(II)-mediated C–C bond-forming reactions have rarely been achieved in a well-defined manner.^[1] This seems curious since the Pd^I–Pd^I complexes are readily accessible and the Pd^{II} and Pd⁰ oxidation states also exist.^[2] One reason could be that relatively nonlabile auxiliary ligands are used to support the Pd–Pd bond (for example, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, RNC)^[2] so that only a single molecule of unsaturated compounds such as alkynes can be bound (Scheme 1).^[3] We sought Pd–Pd complexes that can provide multiple coordination sites for substrate molecules. We report here a facile, regioselective coupling of a terminal alkyne onto the Pd–Pd bond of $[\text{Pd}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ (**1**),^[4] a dipalladium complex with more labile ligands, to generate an electrophilic μ -1 κ C1,4:2 κ C1,4-butenediylidene framework.

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