altered biological properties. This synthesis now provides the opportunity to develop a new class of non-carbohydrate and non-peptidic inhibitors of leukocyte adhesion to endothelial cells.

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[13] **1**: $R_f = 0.40$ (CHCl$_3$/MeOH 9:1); $R_f = 0.14$ (Et$_2$O); ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 7.20$ (dd, $^3J = 15$, $^3J = 10$ Hz, 1H), 6.88 (dd, $^3J = 15$, $^3J = 10$ Hz, 1H), 6.52 (dd, $^3J = 15$, $^3J = 10$ Hz, 1H), 6.20 (m, 5H), 6.06 (m, 1H), 6.02 (m, 1H), 5.80 (m, 2H), 5.52 (dd, $^3J = 15$, $^3J = 6$ Hz, 1H), 5.41 (d, $^3J = 15$ Hz, 1H), 4.20 (m, 1H), 3.31 (m, 1H), 2.96 (m, 1H), 2.40 (m, 1H), 2.32 (m, 1H), 2.24 (m, 1H), 1.02 (d, $^3J = 7$ Hz, 3H); MS (ESI, positive mode, MeOH/CHCl$_3$ 2:1): 312 [M^++H]; MS (ESI, negative mode, MeOH/CHCl$_3$ 2:1): 345 [M^-+Cl], 310 [$M^- -$ H]. To further support the good agreement of the NMR data recorded for the olefin region of (9*S*,18*R*)-**1** with the values measured for the natural stereoisomer of cyclamenol A, we have calculated the differences in total energy and total steric energy for the 12,13-*cis* and the 12,13-*trans* isomers of (9*S*,18*R*)-cyclamenol. The calculations were performed with the PM3 and the MM+ programs implemented in HyperChem 5.02. The semiempirical calculations at the PM3 level revealed a difference in total energy of $\Delta H_{\mathrm{total}}(12,13\text{-}cis) - \Delta H_{\mathrm{total}}(12,13\text{-}trans) = -37.2\ \mathrm{kJ\,mol^{-1}}$ and the force field calculations at the MM+-level yielded a difference in total steric energy of $\Delta H_{\mathrm{total}}(12,13\text{-}cis) - \Delta H_{\mathrm{total}}(12,13\text{-}trans) = -49.7\ \mathrm{kJ\,mol^{-1}}$. Thus, the 12,13-*cis* isomer is energetically much more favored than the corresponding *trans* isomer, and the formation of the *trans* isomer can be ruled out for energetic reasons. In addition, for related tetraene and polyene systems it is known that the energetically less favorable isomers spontaneously isomerize to the more stable analogues: a) K. C. Nicolaou, S. E. Webber, J. Ramphal, Y. Abe, *Angew. Chem.* **1987**, *99*, 1077–1079; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1019–1021; b) M. B. Andrus, S. D. Lepore, *J. Am. Chem. Soc.* **1997**, *119*, 2327–2328; c) B. Crousse, M. Alami, G. Linstrumenelle, *Tetrahedron Lett.* **1995**, *36*, 4245–4248. In addition, the ^{1}H NMR spectrum of the *O*-silylated thionocarbonate obtained from diol **18** displays a coupling constant of 7 Hz for the two CH(OCS) signals of the five-membered ring. This indicates that the two hydrogen atoms are *cis*-oriented (in related compounds coupling constants of 6.5–7.8 Hz are found: d) P. S. Manchand, P. S. Belica, M. J. Holman, T. Huang, H. Maehr, S. Y.-K. Tam, R. T. Yang, *J. Org. Chem.* **1992**, *57*, 3473–3478; e) I. Maeba, N. Morishita, P. Francom, M. J. Robins, *J. Org. Chem.* **1998**, *63*, 7539–7541; f) De Angelis, M. Marzi, P. Minetti, D. Misiti, S. Muck, *J. Org. Chem.* **1997**, *62*, 4159–4161; g) M. G. Lester, G. M. P. Giblin, G. G. A. Inglis, P. A. Procopiou, B. C. Ross, N. S. Watson, *Tetrahedron Lett.* **1993**, *34*, 4357–4360. Since the elimination of thionocarbonates to olefins is known to be a stereospecific *syn*-elimination the *cis*-olefin must have been formed.

[14] We are grateful to Dr. B. Fugmann, Bayer AG, for samples of natural cyclamenol A.

Crossed Condensation of Two Different Hydrosulfido-Bridged Dinuclear Complexes: Structures and Reactivities of TiRu$_3$S$_4$ Cubane-Type Sulfido Clusters**

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Rational construction of sulfido clusters has been a major objective in synthetic inorganic chemistry because these clusters have possible relevance to metalloenzymes and

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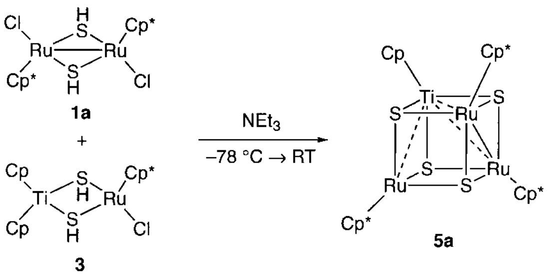
nonmolecular metal sulfide materials including hydrodesulfurization catalysts.[1] We have recently demonstrated that the self-condensation of the hydrosulfido-bridged dinuclear complexes [Cp*MCl(μ_2-SH)$_2$MClCp*] (**1a**: M = Ru; **1b**: M = Rh; **1c**: M = Ir; Cp* = η^5-C_5Me_5) in the presence of a base affords a series of cubane-type sulfido clusters [(Cp*M)$_4$(μ_3-S)$_4$] (**2a**: M = Ru;[2] **2b**: M = Rh;[3] **2c**: M = Ir[3]). Interestingly, even cyclopentadiene is eliminated from the hydrosulfido-bridged heterobimetallic complex [Cp$_2$Ti(μ_2-SH)$_2$RuClCp*] (**3**; Cp = η^5-C_5H_5) to give the heterobimetallic cluster [(CpTi)$_2$(Cp*Ru)$_2$(μ_3-S)$_4$] (**4**).[4] As an extension of these studies, we describe here the crossed condensation of the two different hydrosulfido-bridged dinuclear complexes **1a** and **3**, which results in the formation of the novel TiRu$_3$S$_4$ cubane-type sulfido cluster [(CpTi)(Cp*Ru)$_3$(μ_3-S)$_4$] (**5a**).

When an excess of triethylamine was added to a 1:1 mixture of **1a** and **3** at −78 °C, the dark reddish brown solution immediately changed to deep violet, which progressed further to dark brown as the solution was warmed to room temperature. The ^{1}H NMR spectrum of the reaction mixture indicated that the crossed condensation product **5a** was predominantly formed along with trace amounts of self-condensation products **2a** and **4**. Subsequent chromatographic workup and recrystallization afforded the cubane-type sulfido cluster **5a** in 71 % isolated yield [Eq. (1)]. An X-ray analysis confirmed the TiRu$_3$S$_4$ cubane-type structure of **5a** (Figure 1).[5] The molecule has an approximate mirror plane bisecting the Ru(1)–Ru(2) vector. As predicted by the effective atomic number (EAN) rule, the 64-electron cluster **5a** has one Ru–Ru and three Ti–Ru bonds. The Ti–Ru distances (mean 2.996 Å) are comparable to those for the Ru→Ti dative bonds in the Ti$_2$Ru$_2$S$_4$ cluster **4** (mean 2.935 Å).[4] The Ru(1)–Ru(2) distance of 2.8215(5) Å is also consistent with the Ru–Ru bond order of unity, whereas the other Ru–Ru distances (mean 3.614 Å) preclude the presence of the direct bonding interaction between these Ru atoms. This metal-metal bonding scheme sharply contrasts with that in the electron-deficient, early-late heterobimetallic cluster **4**, which has 60 electrons and only four Ru→Ti dative bonds but no significant Ru–Ru or Ti–Ti interactions.[4] Mixed-metal cubane-type[7] or cuboidal clusters[8] related to **5a** have been reported recently. Cluster **5a** also provides a still-limited example of cubane-type clusters with a MM'$_3$S$_4$ core and four η^5-C_5R_5 ligands.[9]



(1)

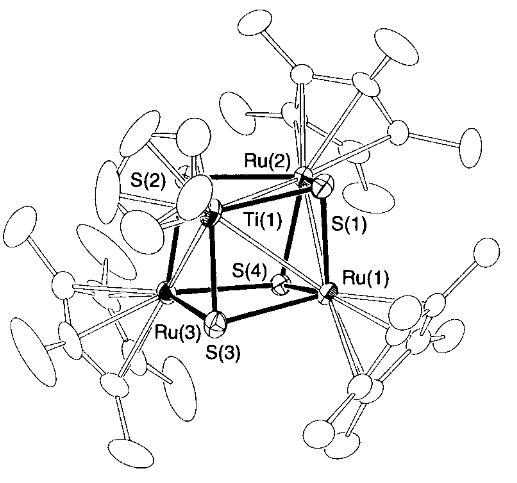
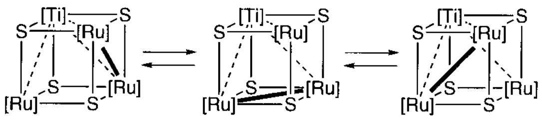


Figure 1. Molecular structure of **5a**. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ti(1)-Ru(1) 2.9876(8), Ti(1)-Ru(2) 3.0158(8), Ti(1)-Ru(3) 2.9854(8), Ru(1)-Ru(2) 2.8215(5), Ru(1)-Ru(3) 3.612(1), Ru(2)-Ru(3) 3.616(1).

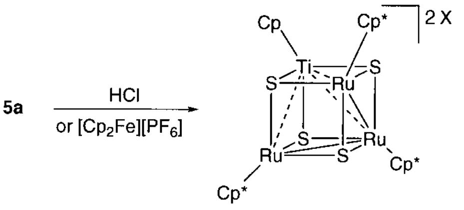
Variable-temperature ^{1}H NMR measurements indicated the mobility of the Ru–Ru bond in **5a**, as shown in Scheme 1. In agreement with the solid-state structure of **5a**, the resonances for the Cp* groups appear as two singlets in an intensity ratio of 2:1 at −50 °C. These two signals coalesce at 0 °C and appear as a sharp singlet at 80 °C. The resonance for the Cp group appears as one sharp singlet throughout the measurements. The activation parameters, estimated by fitting the simulated spectra to the observed ones, are $\Delta H^{\neq} = 53 \pm 4\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = -5 \pm 14\,\mathrm{J\,mol^{-1}\,K^{-1}}$ with $\Delta G^{\neq} = 55 \pm 6\,\mathrm{kJ\,mol^{-1}}$ (0 °C). Rauchfuss and co-workers have already reported similar fluxional behavior ascribed only to the arrangement of the metal-metal bond(s) for homometallic ruthenium[10] or iridium[11] clusters.



Scheme 1. Mobility of the intermetallic bond in **5a**. [Ti] = CpTi, [Ru] = Cp*Ru.

On the other hand, similar treatment of the rhodium or iridium analogue **1b** (or **1c**) with **3** afforded the mixture of **2b** (or **2c**), [(CpTi)(Cp*Ru)(Cp*M)$_2$(μ_3-S)$_4$] (**5b**: M = Rh; **5c**: M = Ir), and **4**. For example, the ratio of the clusters **2b**, **5b**, and **4** produced was approximately 5:12:7 as estimated from the ^{1}H NMR spectrum of the crude product. Attempts to separate these clusters by column chromatography or fractional recrystallization have failed.

We have already found that the electron-deficient Ti$_2$Ru$_2$S$_4$ cluster **4** is oxidized by HCl to afford the distorted cubane-type cluster [(CpTiCl$_2$)(CpTi)(Cp*Ru)$_2$(μ_3-S)$_4$], in which the chlorine atoms are coordinated to one of the titanium atoms to mitigate the electron deficiency of this atom.[4b] The electron-precise TiRu$_3$ cluster **5a** was oxidized by HCl in a different manner. Thus, treatment of **5a** with an excess of HCl gas in toluene afforded the dicationic cluster [(CpTi)(Cp*Ru)$_3$(μ_3-S)$_4$]Cl$_2$ (**6a**) as shown in Equation (2). Cluster **5a** was also oxidized with two equivalents of [Cp$_2$Fe][PF$_6$] to give the PF$_6^-$ salt **6b**. An X-ray analysis of **6a**·HCl·H$_2$O·MeCN



(2)

6a: X = Cl
6b: X = PF_6

clearly demonstrated the ionic nature of **6a** (Figure 2).[5] The two-electron oxidation resulted in the formation of one more Ru–Ru bond than **5a**: the Ru(1)–Ru(2) and Ru(2)–Ru(3) distances (mean 2.845 Å) are congruent with the presence of Ru–Ru bonds, whereas the Ru(1)–Ru(3) distance (3.513(1) Å) is comparable to the nonbonding contacts in **5a**. The Ti–Ru distances (mean 2.984 Å) suggest the presence of three Ru→Ti dative bonds.[12] These observations for the 62-electron clusters **6** are consistent with the EAN rule. Like **5a**, clusters **6a** and **b** exhibit fluxional behavior in solution; the simulations gave activation parameters of $\Delta H^{\neq} = 60 \pm 6\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = 6 \pm 20\,\mathrm{J\,mol^{-1}\,K^{-1}}$ with $\Delta G^{\neq} = 58 \pm 8\,\mathrm{kJ\,mol^{-1}}$ (–10 °C) for **6b**.

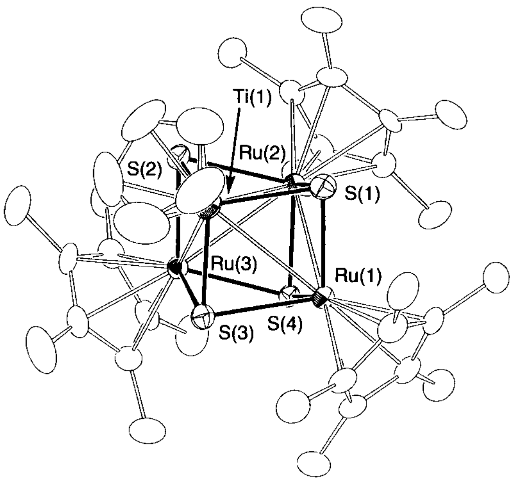


Figure 2. Structure of the cationic part of **6a**·HCl·H_2O·MeCN. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ti(1)-Ru(1) 3.012(2), Ti(1)-Ru(2) 2.934(2), Ti(1)-Ru(3) 3.007(2), Ru(1)-Ru(2) 2.8386(9), Ru(1)-Ru(3) 3.513(1), Ru(2)-Ru(3) 2.850(1).

Condensation of preassembled metal-sulfur aggregates has attracted increasing attention because it provides a rational pathway to metal-sulfido clusters with higher nuclearity. Indeed, clusters with symmetrical structural motifs such as polycubanes,[13] raft-type,[14] and hexanuclear octahedral frameworks relating to Chevrel phases[14a] have reasonably been prepared through this method. However, crossed condensation of different polynuclear units remains undeveloped. In the present study, this synthetic strategy has successfully been applied to the synthesis of cubane-type clusters with $M'M_3S_4$ cores, which have been previously prepared only by using a self-assembly approach[15] or incorporation of a heterometal into the preassembled M_3S_4 cores.[16] Further investigation on syntheses of mixed-metal cubane-type sulfido clusters through this synthetic pathway as well as the reactivities of the $TiRu_3S_4$ clusters **5a** and **6** is now under way.

Experimental Section

5a: To a mixture of **1a** (416.0 mg, 0.682 mmol) and **3** (352.6 mg, 0.683 mmol) in THF/CH_2Cl_2 (40 mL/40 mL) was added triethylamine (1.5 mL, 11 mmol) at –78 °C, and the mixture was slowly warmed to room temperature with stirring. After removal of the solvent in vacuo, the resultant red-brown oil was extracted with benzene. The extract was then subject to chromatography on alumina with benzene, followed by recrystallization from CH_2Cl_2/CH_3OH (10 mL/50 mL). The dark red-brown crystals that formed were filtered off and dried in vacuo (463.0 mg, 71 %). ^1H NMR (400 MHz, $[D_8]$toluene, –50 °C, TMS): $\delta = 5.94$ (s, 5H, C_5H_5), 1.91 (s, 15H, C_5Me_5), 1.50 (s, 30H, C_5Me_5); elemental analysis for $C_{35}H_{50}Ru_3S_4Ti$: calcd: C 44.24, H 5.30; found: C 43.88, H 5.36. For **5b**: ^1H NMR (400 MHz, $[D_6]$benzene, 18 °C, TMS): $\delta = 6.07$ (s, 5H, C_5H_5), 1.84 (s, 15H, RuC_5Me_5), 1.54 (s, 30H, RhC_5Me_5). For **5c**: ^1H NMR (400 MHz, $[D_6]$benzene, 18 °C, TMS): $\delta = 6.02$ (s, 5H, C_5H_5), 1.82 (s, 15H, RuC_5Me_5), 1.55 (s, 30H, IrC_5Me_5).

6a: Through a solution of **5a** (52.8 mg, 0.0556 mmol) in toluene (5 mL) was bubbled HCl gas for 5 min, and the mixture stirred for 2 h. The resultant brown suspension was evaporated to dryness in vacuo. Recrystallization of the residue from MeCN/Et_2O (3 mL/17 mL) afforded **6a**·HCl·H_2O·MeCN as dark red-brown crystals (50.5 mg, 81 %). ^1H NMR (400 MHz, $[D_2]$dichloromethane, –50 °C, TMS): $\delta = 6.01$ (s, 5H, C_5H_5), 1.91 (s, 15H, C_5Me_5), 1.80 (s, 30H, C_5Me_5); elemental analysis for $C_{37}H_{56}Cl_3NORu_3S_4Ti$: calcd: C 39.80, H 5.06, N 1.25, Cl 9.53; found: C 39.69, H 5.13, N 1.36, Cl 9.91.

6b: A mixture of **5a** (65.6 mg, 0.0690 mmol) and $[Cp_2Fe][PF_6]$ (45.9 mg, 0.139 mmol) was dissolved in CH_2Cl_2 (10 mL) and stirred for 12 h. After removal of the solvent in vacuo, the resultant red-brown powder was washed with Et_2O. Recrystallization from MeCN/Et_2O (3 mL/17 mL) afforded **6b**·0.5MeCN·0.5Et_2O as red-brown crystals (78.6 mg, 88 %). ^1H NMR (400 MHz, $[D_2]$dichloromethane, –50 °C, TMS): $\delta = 6.01$ (s, 5H, C_5H_5), 1.81 (s, 15H, C_5Me_5), 1.78 (s, 30H, C_5Me_5); elemental analysis for $C_{38}H_{56.5}F_{12}N_{0.5}O_{0.5}P_2Ru_3S_4Ti$: calcd: C 35.17, H 4.39, N 0.54; found: C 35.25, H 4.39, N 0.78.

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[4] a) S. Kuwata, M. Hidai, *Chem. Lett.* **1998**, 885–886; b) S. Kabashima, S. Kuwata, M. Hidai, *J. Am. Chem. Soc.* **1999**, *121*, 7837–7845.

[5] Structure solution and refinements were performed by using the teXsan program package, see ref. [6]. Crystal data for **5a**: $C_{35}H_{50}Ru_3S_4Ti$, $M_r = 950.14$, crystal dimensions $0.1 \times 0.2 \times 0.5$ mm, triclinic, $P\bar{1}$, $a = 10.557(1)$, $b = 11.5116(9)$, $c = 17.152(2)$ Å, $\alpha = 78.371(8)^\circ$, $\beta = 77.116(10)^\circ$, $\gamma = 69.960(8)^\circ$, $V = 1891.0(4)$ Å^3, $\rho_{\mathrm{calcd}} = 1.669\,\mathrm{g\,cm^{-3}}$, $2\theta_{\max} = 55^\circ$, scan mode ω-2θ, room temperature, $F(000) = 956$, $\mu = 16.23\,\mathrm{cm^{-1}}$, Rigaku AFC7R diffractometer, $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.7107$ Å), graphite monochromator, 9158 measured reflections, Lorentz polarization and absorption corrections (transmission factors: 0.8789–0.9982), full-matrix least-squares refinement based on $|F|$, 389 parameters, H atoms included with fixed parameters, $R = 0.029$ and $R_w = 0.027$ ($w = 1/\sigma^2 F_o$) for 6701 observed reflections [$I > 3\sigma(I)$], max./min. residual electron density 0.28/–0.26 e$^-$ Å^{-3}. Crystal data for **6a**·HCl·H_2O·MeCN: $C_{37}H_{56}Cl_3NORu_3S_4Ti$, $M_r = 1116.57$, crystal dimensions $0.2 \times 0.3 \times 0.7$ mm, monoclin-

ic, space group $P2_1/c$, $a = 14.627(2)$, $b = 14.762(2)$, $c = 20.654(2)$ Å, $\beta = 97.923(4)°$, $V = 4417.1(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.679$ g cm^{-3}, $2\theta_{max} = 55°$, room temperature, $F(000) = 2248$, $\mu = 15.81$ cm^{-1}, Rigaku RAXIS-RAPID imaging plate area detector, $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å), graphite monochromator, 17753 measured reflections, Lorentz polarization and absorption corrections (transmission factors: 0.3044–0.7289), full-matrix least-squares refinement based on $|F|$, 461 parameters, H atoms except for those for HCl/H$_2$O included with fixed parameters, $R = 0.052$ and $R_w = 0.076$ ($w = 1/\sigma^2F_o$) for 6248 observed reflections [$I > 3\sigma(I)$], max./min. residual electron density 0.78/–1.26 e$^-$ Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134168 (**5a**) and -134169 (**6a** · HCl · H$_2$O · MeCN). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Synthesis of Mixed-Metal High-Nuclearity Clusters by Fusion of Anionic Ruthenium Carbido Clusters through Palladium Units

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High-nuclearity cluster complexes, in particular heterometallic clusters, have attracted considerable interest because of their diverse properties.[1, 2] One example is their application as precursors for metal dispersions with discrete metal atom composition, which may be useful as heterogeneous catalysts.[3] The fusion of two smaller cluster units through different metal atoms should provide a straightforward method to increase the nuclearity of carbonyl clusters efficiently. A large number of fusions of transition metal clusters by treatment of the cluster anions with cations or halides of Cu,[4] Ag,[5, 6] Au,[4e, 7] and Hg[7d, 8] to give a "sandwiching" of these metal atoms between two cluster units have been reported. In contrast, the reactions of cluster anions with cation or halide of Group 10 transition metals have been known to give giant clusters comprising two different transition metals, for example, $[Ni_{38}Pt_6(CO)_{48}(H)_{6-n}]^{n-}$,[9] $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$,[10] $[Ni_{36}Pt_4(CO)_{45}]^{6-}$,[11] and $[Fe_6Pd_6(CO)_{24}H]^{3-}$.[12] In these examples, considerable fragmentation and recombination of the original cluster component appear to be the important factors. Herein we report on the coupling of ruthenium carbido carbonyl clusters through palladium species to give high-nuclearity Ru/Pd mixed-metal complexes of "sandwich cluster" type structure. This is similar to the many cases of Group 11 and 12 metals as linking agents, rather than the unpredictable cluster formation by fragmentation and spontaneous assembly pathways. Incorporation of a Group 10 transition metal as a linking agent in sandwiching products should greatly widen the scope of the fusion route as a method for the rational synthesis of large heterometallic clusters, particularly in terms of their application as potential precursors for tailored alloy catalysts. This investigation is significant in that ruthenium and palladium are utilized as heterogeneous catalysts in a wide variety of industrial reactions.[13]

Treatment of the pentanuclear ruthenium carbido anion $[Ru_5C(CO)_{14}]^{2-}$ (cation: PPN = $N(PPh_3)_2{}^+$) with with two equivalents of $[Pd(C_3H_5)Cl]_2$ in THF at room temperature for 12 h gave dark red crystals of a neutral cluster with the composition $[Pd_8Ru_{10}C_2(CO)_{27}(C_3H_5)_4]$ (**1**) in 52% yield. X-ray structural analysis (Figure 1) revealed that the molecule has two pseudo mirror planes, one of which passes through Pd2, Pd5, Ru11, and Ru21 and the other through Pd7, Pd8, C20, O21, C8, and C11.

The Pd_8 core, which is flanked on each side by a square-pyramidal Ru_5 core, consists of two coplanar fused squares, Pd1-Pd2-Pd5-Pd4 and Pd2-Pd3-Pd6-Pd5, and two Pd atoms, Pd7 and Pd8, which cap each of the squares from the same

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